Laboratory Directed Research and Development (LDRD) on Mono-uranium Nitride Fuel Development for SSTAR and Space Applications

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U.S. Department of Energy

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February 13, 2006

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FY2005 FINAL REPORT

LABORATORY DIRECTED RESEARCH AND DEVELOPMENT (LDRD) ON MONO-URANIUM NITRIDE FUEL DEVELOPMENT FOR SSTAR AND SPACE APPLICATIONS

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13 February 2006

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1.   EXECUTIVE SUMMARY

The US National Energy Policy of 2001[1] advocated the development of advanced fuel and fuel cycle technologies that are cleaner, more efficient, less waste-intensive, and more proliferation resistant. The need for advanced fuel development is emphasized in on-going DOE-supported programs, e.g., Global Nuclear Energy Initiative (GNEI)[2], Advanced Fuel Cycle Initiative (AFCI)[3], and GEN-IV[4] Technology Development. The Directorates of Energy & Environment (E&E) and Chemistry & Material Sciences (C&MS) at Lawrence Livermore National Laboratory (LLNL) are interested in advanced fuel research and manufacturing using its multi-disciplinary capability and facilities to support a design concept of a small, secure, transportable, and autonomous reactor (SSTAR)[5]. The E&E and C&MS Directorates co-sponsored this Laboratory Directed Research & Development (LDRD) Project on Mono-Uranium Nitride Fuel Development for SSTAR and Space Applications. In fact, three out of the six GEN-IV reactor concepts consider using the nitride-based fuel, as shown in Table 1.

Table 1. GEN-IV Reactor Concepts

Reactor Type	Neutron Spectrum	Coolant	Temp. (C)	Pressure	Fuel	Fuel Cycle	Size (MWe)	Uses
Gas-cooled fast reactors	fast	helium	850	high	UO_2, UN, or UC	closed, on site	288	electricity
LM*-cooled fast reactors	fast	Pb-Bi	550-800	low	UO_2, UN, or UC	closed, regional	10-150	electricity
Molten salt reactors	epithermal	fluoride salts	700-800	low	UF_4 in salt	closed	1000	electricity
Sodium-cooled fast reactors	fast	sodium	550	low	UO_2, UN, or UC	closed	150-500	electricity
Supercritical-cooled fast reactors	thermal or fast	water	510-550	very high	UO_2	open (thermal)	1500	electricity
Very high temperature gas reactors	thermal	helium	1000	high	UO_2 prism or pebbles	open	250	hydrogen & electricity

* LM – Liquid-Metal (e.g., Pb or Pb/Bi)

SSTAR is a liquid-metal cooled, fast reactor. It uses nitride fuel in a sealed reactor vessel that could be shipped to the user and returned to the supplier having never been opened in its long operating lifetime. This sealed reactor concept envisions no fuel refueling nor on-site storage of spent fuel, and as a result, can greatly enhance proliferation resistance. However, the requirement for a sealed, long-life core imposes great challenges to research and development of the nitride fuel and its cladding. Cladding is an important interface between the fuel and coolant and a barrier to prevent fission gas release during normal and accidental conditions. In fabricating the nitride fuel rods and assemblies, the cladding material should be selected based on its the coolant-side corrosion properties, the chemical/physical interaction with the nitride fuel, as well as their thermal and neutronic properties.

The US NASA space reactor, the SP-100[6] was designed to use mono-uranium nitride fuel. Although the SP-100 reactor was not commissioned, tens of thousand of nitride fuel pellets were manufactured and lots of them, cladded in Nb-1-Zr had been irradiated in fast test reactors (FFTF and EBR-II) with good irradiation results. The Russian Naval submarines also use nitride fuel with stainless steel cladding (HT-9) in Pb-Bi coolant. Although the operating experience of the Russian submarine is not readily available, such combination of fuel, cladding and coolant has been proposed for a commercial-size liquid-metal cooled fast reactor (BREST-300)[8].

Uranium mono-nitride fuel is studied in this LDRD Project due to its favorable properties such as its high actinide density and high thermal conductivity. The thermal conductivity of mono-nitride is 10 times higher than that of oxide (23 W/m·K for UN vs. 2.3 W/m·K for UO_2 at 1000 K)[2] and its melting temperature is much higher than that of metal fuel (2630°C for UN vs. 1132°C for U metal). It also has relatively high actinide density, (13.51 gU/cm^3 in UN vs. 9.66 gU/cm^3 in UO_2) which is essential for a compact reactor core design.

The objective of this LDRD Project is to

- Establish a manufacturing capability for uranium-based ceramic nuclear fuel,
- Develop a computational capability to analyze nuclear fuel performance,
- Develop a modified UN-based fuel that can support a compact long-life reactor core,
- Collaborate with the Nuclear Engineering Department of UC Berkeley on nitride fuel reprocessing and disposal in a geologic repository.

Manufacturing of Mono-uranium Nitride Fuel Pellets

Uranium mono-nitride fuel pellets and the modified nitride-based uranium fuel pellets are manufactured at the Lawrence Livermore National laboratory (LLNL) by carbothermic reduction of oxides in a controlled glove box environment. Figure 1 shows the process flow diagram for UN fuel manufacturing. Facilities to support the manufacture of nitride-based fuel pellets were activated and upgraded in support of this project and remain in operation in B-241 at LLNL.

At the start of this LDRD Project and in support of the fuel manufacturing effort, a glove box from B-332 was moved into the fuel-manufacturing laboratory in B-241. Installation of the glove box and the applicable equipment was completed. This installation included a furnace with heat rating up to 1650 C, a hydraulic press which can press "green UN fuel pellets", and glove-box control system (Dri-train) to ensure the purity of the box atmosphere. These facilities are designed to provide the capabilities for controlling nitride synthesis and sintering process parameters, allowing evaluation of the manufactured nitride fuel product with respect to desired stoichiometry, density, and grain structure. The glove box arrangement and the dri-train system for the nitrogen glove box are shown in Figure 2 and 3, respectively.

The facilities to support nitride fuel development have been implemented within three primary facility components: glove box, furnace hood, and analysis capabilities (gas analysis cart, distributed data collection, analytical support labs). The glove box provides the capacity for locating all of the non-furnace operations within one dry, clean N_2 atmosphere. It consists of the glove box enclosure, a Dri-train catalytic bed and molecular sieve, and a clean N_2 source. The glove box N_2 atmosphere circulates through the VAC dual bed Dri-train, which removes both oxygen and water contaminants.

Figure 1. Process Flow Diagram for Uranium Nitride Fuel Manufacturing

Process flow diagram:

- UO_2 → Grinding/Blending (12 to 24 h), with C input
- → $UO_2 + 3C = UCN + 2CO(g) + C$ (1500°C) **(100 hours)**, with $N_2(g)$ input and $CO(g)$ output → $UC_yN_{1-y} + C$
- → $C + 2H_2(g) = CH_4(g)$ (1300°C), with <4%H_2(g)/N_2(g) input and CH_4(g) output → UC_yN_{1-y}
- → $UCN + 0.5N_2(g) = UN + C$ (1300°C) **(75 hours total)**, with <4%H_2(g)/N_2(g) input → UN_{1+y}
- → $C + 2H_2(g) = CH_4(g)$ (1300°C), with <4%H_2(g)/N_2(g) input and CH_4(g) output → UN_{1+y}
- → $UN_{1+y} = UN + N_2(g)$ (1300°C) **(75 hours)**, with Ar(g) output → UN
- → Grinding/Blending/Granulation (30 min to 30 h), with N_2(g) or Ar(g) input, and ZrN, HfN, others input
- → Pressing 10 to 30 ksi
- → Sintering (1650°C) (6 to 12 h), with Ar(g) input → Pellets

Figure 2. Nitride glovebox (foreground), furnace hood (background), and gas analysis cart (right). Note: HEPA filtered exhaust.
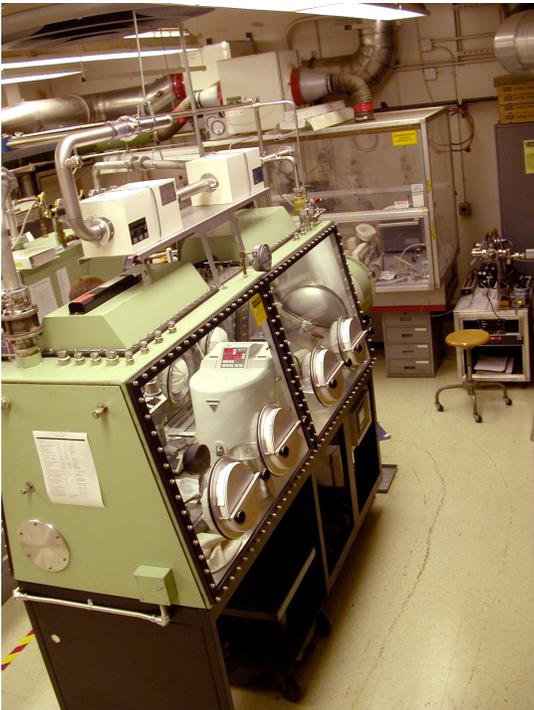
Figure 3. Dri-train system

Once the facility was fully activated, a total of twenty one uranium nitride tests were completed from October 2003 through August 2005. The remaining two months of FY05 were spent in removing the furnace air enclosure and relocating HEPA filter hardware in preparation for the facility furnace upgrade.

A chronological review of the test results provides some insight as to problems encountered and the resulting evolution of the test plan. After the test run on December 2003, it became apparent that longer furnace runs would be needed due to furnace temperature limitations and processing inefficiencies. A series of furnace outages, caused by material loss at the platinum-rhodium thermocouple juncture, were attributed to chemical reaction of the thermocouple with the furnace reducing gas environment. A fully sheathed replacement thermocouple was identified and implemented. The sheathed thermocouple completely eliminated this mode of furnace failure.

The other mode of furnace failure, tube cracking, was minimized but not fully eliminated through use of gradual thermal ramping (1.5 ^{o}C per minute), careful use of thermal insulation to maintain an acceptable thermal gradient on the tube, and frequent furnace tube replacement. Furnace tube failure usually resulted in leakage of air into the furnace tube, converting of all nitride back to oxide.

Once these issues were managed, run durations were increased to allow for the full chemical reaction among the process constituents, to determine the "end of test" sample composition, and to adjust the initial carbon (C) fraction to minimize excess UO_2 or C remnants. The goal of fully reacting all batch constituents was approached but not verified because of the limitations of the furnace temperature and the fraction of H_2 process gas mixture. Working within these limitations, only low sintered density of the "end of test" material, with respect to full theoretical density, even with run durations in excess of 250 hours was achieved. The resulting UN fuel pellets were also not of sufficient purity to permit thermal conductivity measurement within the instrument measurement range, defined by the thermal conductivity of uranium nitride, nominally 15 W/m-^{o}K at room temperature.

Computational Analysis of UN Fuel Performance

Fast reactor fuel performance computer codes, LIFE4Rev1 and SIEX3 were first acquired from DOE's Nuclear Fuel Cycle Software Center. These codes are "Advanced Technology", hence, their acquisition and distribution are controlled by the DOE/NEST office. These codes were written for fast reactor using oxide-based fuel, and hence, significant modifications to the codes including those material properties (as shown in Figure 4) are required for use to simulate nitride fuel performance.

Figure 4. Material property correlations for UN[3]
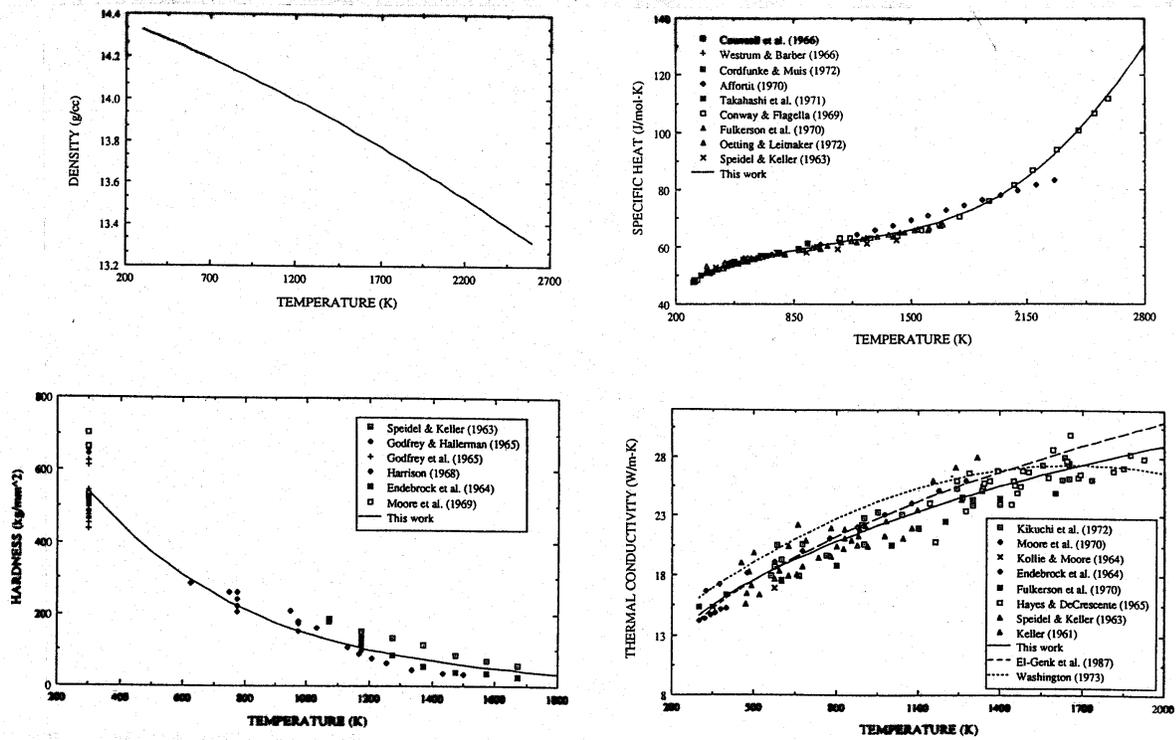
To avoid a significant effort in code modification, the nitride fuel performance code developed for the SP-100 space reactor project, SPACEPIN was acquired and made operational at LLNL. The code is a semi-empirical code which contains thermal, structural, fuel swelling, fission gas release, nitrogen migration, and other fuel pellet performance prediction models. The current version of the code uses calibration constants set to minimize the error in the predictions of test data for a database that bounds the SP-100 performance requirements. Additional development is needed to add the theoretical capability to extrapolate the predictions beyond those of the SP-100 database.

The SPACEPIN code was used to analyze the SP-100 fuel pellet irradiation. The conditions are:

UN fuel with OD of 0.3" and 11.5" long,
Fuel density of 96% theoretical density (T.D.) and U-235 of 95%,
PWC-11 clad with Re liner,
Liner heat generation rate of 154 W/cm.

The burn-up profile of the SP-100 fuel pellet irradiation and the irradiated cladding strain (in %) were calculated by SPACEPIN and shown in figure 5 and 6, respectively. Results of the SPACEPIN calculations (fission gas release, etc.) indicated good agreement with SP-100 fuel pellet irradiation data. Results of the cladding strain (in %) of UN fuel irradiation calculated by SPACEPIN were compared with those calculated by others using SIEX3. The comparison was shown in Figure 7.

Figure 5. Burn-up Profile of the SP-100 Fuel Pellet, Calculated by SPACEPIN
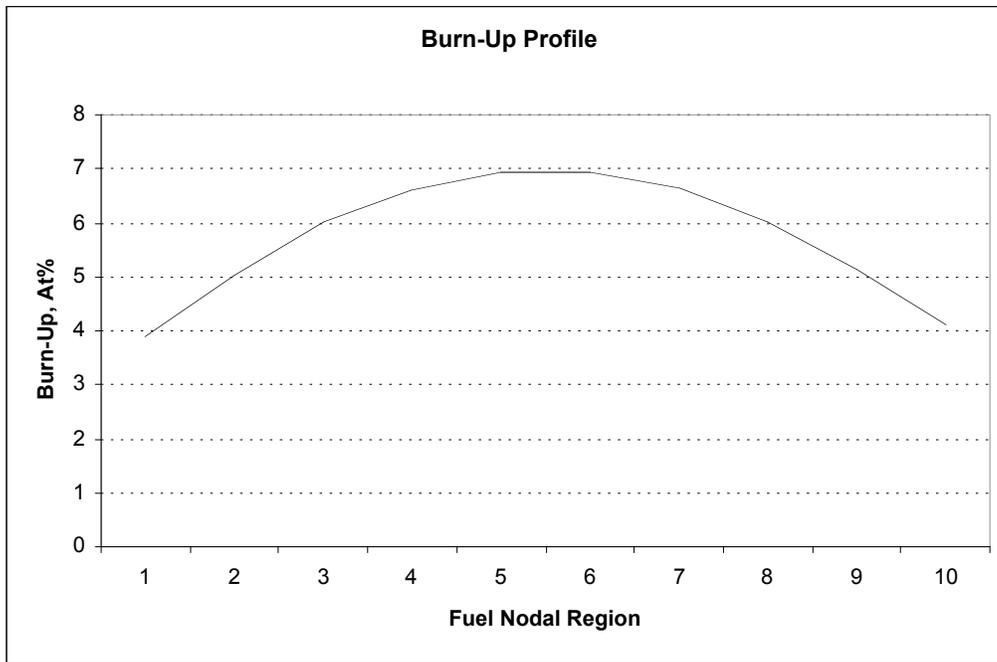
Figure 6. Cladding Strain of UN Fuel Irradiation, Calculated by SPACEPIN

Figure 7. Comparison of Cladding Strain of UN Fuel Irradiation Calculated by SPACEPIN and SIEX3

Peak Radial Temperature Profiles
For Mixed Nitride and Metal Fuels
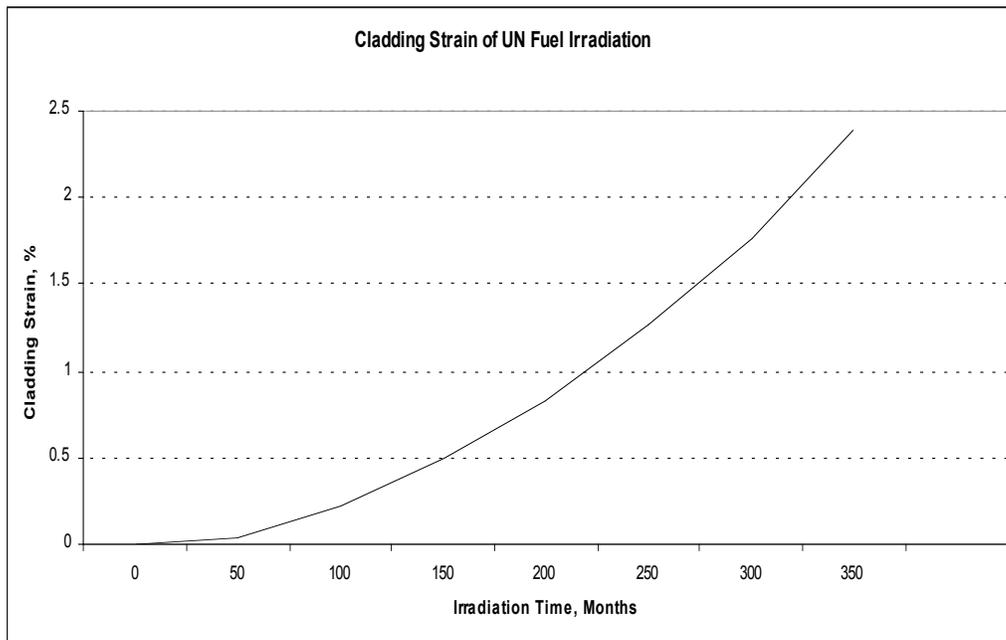
Peak Cladding Strains
For Mixed Nitride and Metal Fuels

——— Calculated by SPACEPIN
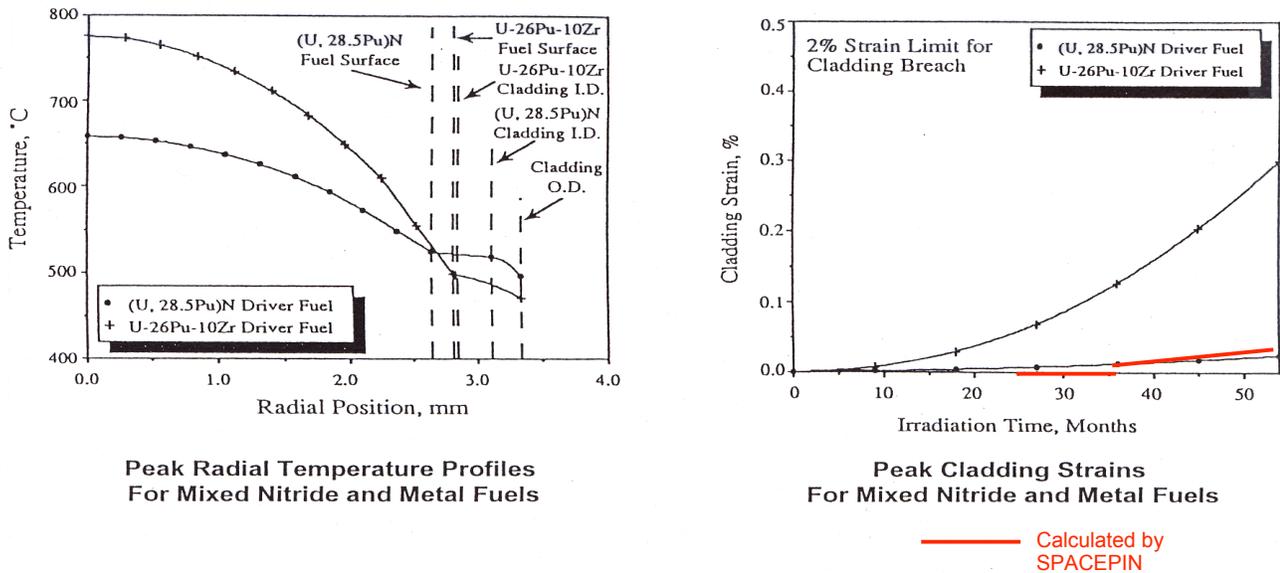
Ref.: W. F. Lyon, et.al., "Performance analysis of a mixed nitride fuel system for an advanced liquid metal reactor," ANS Meeting, November 11-15, 1990, Washington DC.

To enhance the computational capability in reactor code neutronic analysis, the computer code, MONTEBURNS is also acquired. MONTEBURNS consists of two codes: MCNP for particle transport calculations and ORIGEN2 for fuel depletion calculation.

The experience accumulated in using these computer codes (MONTEBURNS, MCNP, ORIGEN2, SPACEPIN, LIFE4REV1 and SIEX3) would enhance our simulation and modeling capability in reactor neutronic and fuel performance analysis.

Development of Modified Nitride-Based Fuel Pellets

This LDRD project centers on the manufacturing and evaluation of modified uranium nitride fuels imbedded with other chemical additives to enhance the fuel properties to achieve long core life with a compact reactor design. The primary factors that affect the selection of the reactor fuel are compactness, long-life, proliferation resistance, fuel safety, and waste management. For a modified nitride-based fuel to be selected over pure mono-uranium nitride fuel, it must be superior in several of these factors and comparable in the remaining factors. The focus of the project is on potential benefits of adding group IIIB nitrides (*e.g.* ZrN, and/or HfN) to the base UN fuel.

A mixture of HfN and UN, in a mass ratio of 3:1 was manufactured on December 13, 2005. The produced hard sintered pellets were significantly less dense than full theoretical density, because of the limitations of the furnace temperature and the fraction of H_2 process gas mixture. The modified UN fuel pellets were also not of sufficient purity to permit thermal conductivity measurement.

Although a fully dense modified UN fuel pellet was not successfully manufactured, the optimum compositions for the modified UN fuel were developed based on the selection criteria. Table 2 summarizes the four parameters against the five selection criteria. A plus (+) means that the

parameter is a slight benefit for that criteria and a minus (-) means that that parameter is a slight detriment to that factor. A zero indicates little or no effect. A double plus indicates a large beneficial effect and a double minus indicates a large detrimental effect.

Table 2. Summary Fuel Selection Criteria

Metric	Enrich.	UN	ZrN	HfN
Compactness	+	0	+	-
Long-Life	++	+	--	+
Prolif. Res.	--	-	+	+
Fuel Safety	0	--	++	++
Waste Man.	0	-	+	+

Given these criteria, four compositions are suggested for further study in Table 3. Case 1 is pure UN with maximum allowable enrichment of ^{235}U. Case 2 is the reference case of UN with 10% enrichment of ^{235}U. Case 3 is an intermediate case with a limited amount of ZrN and HfN added. Ratio of Hf-to-^{235}U is chosen to be 1-to-1. Case 4 is the limiting case where the maximum amount of ZrN is added while limiting the ^{235}U enrichment to 20%. Again the ratio of Hf-to-^{235}U is chosen to be 1-to-1.

Table 3. Selected Compositions for Further Study

	^{235}UN	^{238}UN	ZrN	HfN
Case 1	20	80	0	0
Case 2	10	90	0	0
Case 3	10	70	10	10
Case 4	10	40	40	10

Compositions are given in an atomic or molar basis.

A Record of Invention (ROI, IL-11278) on "Modified Nitride Fuel for Compact and Long-Life Reactors" was filed to the LLNL Patent Office in November 2003.

Collaborate with the Nuclear Engineering Department of UC Berkeley

Collaborate with Prof. Joonhong Ahn of the Nuclear Engineering Department at UC Berkeley on analysis for reprocessing of irradiated UN fuel and for disposing the nitride-based nuclear fuel in a geologic repository was initiated in the FY2005.

The following areas of work are to be addressed by the UCB team:

Task 1: Preliminary literature survey for (1) reprocessing of irradiated mono-nitride fuel and for (2) geochemical reactions of nitride fuel with groundwater

Task 2: Analyses on reprocessing process for mono-nitride fuel

Task 3: Analyses on dissolution mechanisms of nitride fuel in geologic environment to evaluate performance in a geologic repository.

Task 4: Prepare input for the LDRD final report. The UCB study report will be combined with the reports on other activities in the project.

Results of the investigation by the UCB team are summarized below:

For reprocessability, a pyrochemical process method is considered because evolution and recycle of N^{15} gas can be handled. A simplified model reprocessing scheme has been analyzed for the separation of uranium mono-nitride fuel from cerium mono-nitride with a multi-stage extraction system. The distribution coefficient obtained from an optimized single-stage extraction system has been utilized as input data for a multi-stage extraction system. With 10 stages, the overall purity of the recovered uranium was 98.9% in the multi-stage extraction system with a net uranium recovery of 79%.

For repository performance, the dissolution rate for UN would be much lower than that for U metal but higher than that of uranium silicide. The reported high dissolution rates of UN in water at ~ 92°C indicate that UN is not stable in the hot aqueous environment. The numerical evaluation, based on the assumption that the dissolution rate of UN spent fuel is 10 times greater than those for UO_2 and borosilicate glass, indicates that the dissolution of UN spent fuel would complete within the time duration comparable to the half-life of Pu-239.

Thus, while UN may be a good fuel for a reactor that uses a non-aqueous coolant and is operated with a reprocessing option, spent UN fuel will be poor waste form for permanent disposal in a geologic repository because of its reactivity in an aqueous environment.

Exit strategies

- We should pursue funding opportunities with DOE/NE's Advanced Fuel Cycle Initiative, and Global Nuclear Energy partnership Programs on advanced nuclear fuel development to support the advanced burner rector and other GEN-IV reactor concepts.

- DOE/NR/KAPL was interested in funding LLNL to manufacture the simulated fuel (SIMFUEL) for the space reactor fuel and material research. Although the SIMFUEL project did not go forward due to NASA's budget constraint, we should continue to pursue the potential collaboration with DOE/NR laboratories to investigate and develop space nuclear reactor fuel technologies.

- We were contacted by ANL-W (Bruce Hilton) for collaboration with an industrial entity (Westinghouse) in conducting corrosion studies on uranium-nitride fuel. Westinghouse indicates that the UN fuel pellets can be first used in an out-of-pile corrosion experiment. The collaboration could significantly enhance our research and development effort on UN-based fuel.

- We should pursue the collaboration with (1) NASA safety office on space nuclear reactor safety, including UN fuel safety criteria, fuel failure modes, and use of UN EOS in safety analysis and (2) industrial entities, e.g., BWXT, NFS, etc. for R&D activities on advanced fuel technologies used for space nuclear reactors.

2.   HIGHLIGHTS OF ACCOMPLISHMENTS

A manufacturing capability for uranium-based ceramic nuclear fuel was established in LLNL's Fuel Manufacturing Laboratory in B-241. High density oxide fuel including the advanced inert matrix oxide fuel pellets were produced[1] previously with existing equipment. There is a need to upgrade our furnace capability with higher temperature and higher reactant gas fraction in order to produce uranium nitride fuel with the desired stoichiometry, density, and grain structure.

A computational capability to analyze nuclear fuel performance was developed. Industrial-based semi-empirical computer codes (LIFE4Rev1, SIEX3, SPACEPIN, etc.) were acquired and made operational in LLNL computer system. Understanding of the physics models used in these codes should enhance our capability in supporting the multi-scale computational material science development.

Table 1 shows the advanced nuclear fuel development and capability at LLNL.

There were industrial interest and programmatic funding opportunity in our advanced fuel manufacturing capability. Westinghouse and ANL-W (now Idaho National laboratory) were interested in collaborating with us on UN fuel corrosion studies. DOE/NR/KAPL was initiating funding for a SIMFUEL project in LLNL before it was pulled back due to NASA's budget constraint.

Our collaboration with the Nuclear Engineering Department of UC Berkeley on nitride fuel reprocessing and disposal in a geologic repository provided a good opportunity to work with the university faculty and students.

Table 1. Advanced Nuclear Fuel Development and Capability at LLNL

Fuel Type	Applications	Manufacturing Capability	Computational Capability
Mono-uranium Nitride (UN) Fuel	GEN-IV reactor concepts, Space Nuclear Reactor	Making green UN fuel in B-241 Lab. Need to upgrade furnace capability to produce UN fuel with the desired stoichiometry, density, and grain structure	SPACEPIN code can be used to analyze SP-100 irradiated fuel performance data.
Modified Uranium Nitride Fuel	SSTAR, Space Nuclear Reactor	UN fuel with chemical addictives (Zr, Hf, Er, etc)	Need modification of SPACEPIN code for SSTAR
Advanced Oxide Fuel	LWRs, for high burn up	Green pellet made, density >96%TD. Need centerless grinder and new pellet dies to support LWR fuel pellet development	LIFE4Rev1, SIEX3 codes can be used for oxide fuel
Advanced Inert-Matrix (IM) Oxide Fuel	Fast reactors, for non-proliferation applications	Green pellet made with chemical addictives (Zr, Hf), ~94%TD. Need fuel performance data (i.e., irradiation experiment)	Need modification of LIFE4Rev1, SIEX3 for IM oxide fuel

ACKNOWLEDGEMENT

3.   INTRODUCTION

This 3-year LDRD project, started in October 2002 for FY'03, is to research and manufacture an advanced mono-nitride fuel for use in a liquid-metal cooled, <u>S</u>mall, <u>S</u>ecure, <u>T</u>ransportable, <u>A</u>utonomous <u>R</u>eactor (SSTAR), and for space nuclear reactors.

Background

This LDRD project is intended to initiate LLNL's advanced fuel development effort and enhance its capability in material sciences research and manufacturing. The primary goal of the project is to develop and manufacture a modified high thermal conductivity mono-nitrite fuel for the use in compact long-life reactors such as:

- A liquid-metal cooled, <u>S</u>mall, <u>S</u>ecure, <u>T</u>ransportable, <u>A</u>utonomous <u>R</u>eactor (SSTAR)

  The (E&E) Directorate promotes a SSTAR concept intended to provide improved proliferation-resistant characteristics that will make nuclear power more acceptable for worldwide use, including use in developing countries. The Pb-Bi cooled SSTAR incorporates the nitride fuel in a sealed reactor vessel that could be shipped to the user country and returned to the supplier country having never been opened in its long operating lifetime (~30 yhears). The requirements for proliferation-resistance and long-life core impose great challenges to the fuel development.

- A light liquid-cooled reactor designed for space applications

  National Aeronautics and Space Administration (NASA) formed a partnership with DOE/Naval Reactors (NR) to develop space nuclear power reactor and propulsion technologies for space and civilian applications. A light liquid-metal (lithium)-cooled reactor using nitride fuel called SP-100 was designed in the early '90s. Its unique features include long-life core, high reliability and survivability in an outer space environment.

The project focuses on developing LLNL's computational and modeling capability in advanced nuclear fuel performance. Specifically, fuel-performance computational codes will be acquired and modified to analyze the performance of advanced mono-nitride fuel.

Project Objectives

The objective of this LDRD Project is to

- Establish a manufacturing capability for uranium-based ceramic nuclear fuel,
- Develop a computational capability to analyze nuclear fuel performance,
- Develop a modified UN-based fuel that can support a compact long-life reactor core,
- Prepare for a proof-of-principal irradiation experiment on mono-uranium-nitride (UN) fuel pellets, possibly in a test reactor of an industrial entity,
  Collaborate with a UC campus on disposal of nitride-based fuel in a geologic repository.

Project Overview

1. <u>FY'03</u>

- Project started in late October '02.
- Collected a comprehensive list of reference documents on SP-100 fuel, SPR-6, UN fuel manufacturing, UN properties, fuel performance, and Russian experience, and included in the bibliography.

- Acquired Computer codes: LIFE4Rev1 and SIEX3 from DOE's Nuclear Fuel Cycle Software Center. These codes are "Advanced Technology" and hence, their acquisition and distribution are controlled by the DOE/NEST office. These codes were written for oxide-based fuel.
- MONTEBURNS is also acquired to analyze neutron flux and reactor fuel depletion in a reactor core. MONTEBURNS consists of two codes: MCNP for particle transport calculations and ORIGEN for fuel depletion calculation.
- Other relevant codes which could help the building of our analytical capability for nitride fuel are: (1) UNCLE, a code modified from LIFE3 and intended for carbide and nitride fuel, (2) a simplified code used for space reactor SP-100 UN fuel analysis.
- In contact with SP-100 UN fuel designers for information and consultation.

- An MOU was signed between EED and DNT to delegate the safety responsibility associated with the fuel manufacturing process and operation in the Laboratory in B-241 from EED to DNT.
- Safety Review by Hazard Control Department for modification of existing glove boxes was completed.
- A glove box from B-332 was moved into the fuel-manufacturing laboratory in B-241. This glove box was made operational in nitrogen atmosphere and to be used for converting UO_2 to UN by a carbo-thermic reduction method.
- Installation of the glove box and the applicable equipment was completed. This installation included a furnace with heat rating up to 1650 C, a hydraulic press which can provide the pressure to press "green UN fuel pellets", and glove-box control system to ensure the purity of the box atmosphere.
- Visited UN manufacturing line in TA-55 of LANL.

- Two proceedings papers were presented at the ANS Global 2003 Conference in November 2003 in New Orleans:
  - Bart Ebbinghaus, Jor-Shan Choi, and Tom Meier, "*A Modified Nitride-Based Fuel for Long Core Life and Proliferation Resistance*", UCRL-CONF-200563, Nov. 2003.
  - Tom Meier, Bart Ebbinghaus, and Jor-Shan Choi, "*Facilities for Development of Modified Nitride-Based Fuel Pellets*", UCRL-CONF-200564, Nov. 2003.
- Jor-Shan Choi attended the 2nd Workshop on Material Modeling and Simulations for Nuclear Fuels in November in New Orleans, and presented a talk on "Computational Evaluation of Nitride-Based Fuel Performance."

2. <u>FY'04</u>

- Acquired SPACEPIN, a computer code developed and used for the space reactor fuel.
- Analyzed the SP-100 fuel pellet irradiation with SPACEPIN.
- MONTEBURNS was utilized to analyze various reactor configurations and fuel compositions for SSTAR and space reactor applications.

- Develop a modified UN-based fuel that can support a compact long-life reactor core. Based on the criteria of compactness, long-life, proliferation resistance, fuel safety, and waste management, some attractive candidates for a modified nitride-based fuel can be selected and evaluated.
- A Record of Invention (ROI, IL-11278) on "Modified Nitride Fuel for Compact and Long-Life Reactors" was filed to the LLNL Patent Office in November 2003.

- ANL-W (Bruce Hilton) and an industrial entity (Westinghouse) were interested in collaboration for corrosion studies on uranium-nitride fuel. This collaboration affords us the change of venue from the original plan of using the research reactor at McClellan Nuclear Radiation Center (MNRC), operated by UC Davis.

- Facilities supporting development on UN-based fuel materials were installed, tested, qualified for operation, having met all safety and performance requirements for their activation. Qualification tests on essential facilities and equipment (glove box, furnace, and analytical capability) show that these systems meet all performance and operational requirements for this material development effort.
- Data has been collected in two process cycles of facility activation and testing. The initial 2 UN test runs produced a few sintered pellets. The testing and evaluation of the UN process continues, aiming at improvement of density and minimization of impurities of the UN fuel pellets.

3. <u>FY'05</u>

- Use SPACEPIN code for space nuclear reactor fuel performance analysis.
- Fabricate modified uranium-based nitride fuel compositions in B241.
- Collaborate with Prof. Joonhong Ahn of the Nuclear Engineering Department at UC Berkeley on analysis for disposing nitride-based nuclear fuel in a geologic repository.

- DOE/NR laboratories (Knott Atomic Power Laboratory – KAPL) visited our manufacturing Laboratory in May. They were interest in providing funding to us in making simulated fuel (e.g., fuel with imbedded chemical elements of those produced in spent nuclear fuel).
- A new furnace was defined for the proposed SIMFUEL project. Site preparations for the new furnace were completed. This effort involved removing the existing furnace and furnace air enclosure and relocating the HEPA filters that were part of the air enclosure. Completion of this work is shown in Figures 1a and 1b.
- Unfortunately, DOE/NR/KAPL funding was not realized due to NASA's budget constraint.

Figures 1a and 1b – Site of furnace air enclosure and same site following enclosure removal and relocation of HEPA filters for furnace upgrade

- **Complete the final report for this LDRD project**.

4. MANUFACTURING OF MONO-URANIUM NITRIDE FUEL PELLETS

The objective of the research is to manufacture nitride fuel with desired properties in stoichiometry, density, and grain structure and with additives (ZrN and HfN, etc.) for improved stability and high burn-up characteristics. These properties and characteristics are required to support the long-life nitride fuel for a compact reactor core. The thermal conductivity of UN is 10 times higher than that of UO_2 and comparable to that of ZrN and HfN (23 W/m-^{o}K for UN vs. 25 W/m-^{o}K for ZrN, 17 W/m-^{o}K for HfN, 2.3 W/m-^{o}K for UO_2 all at 1000°K). Its melting temperature is much higher than that of metal fuel (2630°C for UN vs. 1132°C for U metal). Uranium mono-nitride also has relatively high actinide density, (13.51 gU/cm3 in UN vs. 9.66 gU/cm^3 in UO2) which is essential for a compact reactor core design.

Process Requirements

Uranium nitride powder for the manufacture of fuel pellets, can be synthesized by a number of processes: metal/nitration, metal hydride/ nitration, metal oxide/carbothermic reduction/nitration, as well as processes starting with metal fluorides or chlorides[1]. High burnup uranium nitride fuel pellets, regardless of the process used in producing the UN powder, should exhibit the following property related characteristics. The UN powder should sinter to greater than 90% full theoretical density. It should produce a predominantly closed pore structure and a relatively large (greater than 40 micron) grain size. The UN should maintain near stoichiometric composition to avoid formation of sesquinitride at one extreme or metallic uranium at the other. Maintained UN stoichiometry and low levels of excess oxygen and carbon impurity, in both powder and final sintered fuel pellet form, are viewed as conducive to achieving sinterability, improved pellet thermal stability and reduced pellet/cladding interaction[6,7,8].

Metal and metal hydride nitration processes typically produce UN having oxygen at levels of 100-700 ppm (parts per million) and carbon at 70-500 ppm. This is considered an acceptable residual oxygen and carbon impurity level for UN[6,7,8]. The UN produced by carbothermic reduction, using the process proposed by Greenhalgh, et.at.[2,3], typically contains 1000 ppm oxygen and 2000 ppm carbon. Muromura and Tagawa modified the carbothermic reduction process by adding a reducing gas component (H_2 or NH_3) that results in impurity levels in the UN (oxygen plus carbon) in the range of 500-1000 ppm combined.[4,5], achieving UN processing capabilities for oxygen and carbon management equivalent to metal and metal hydride nitration. This process, scaled to laboratory-sized operations, can be implemented in a cost effective way. By this criteria, the carbothermic synthesis process was selected as the basis for facility design.

In order to maintain these levels of purity, the handling of powders and pellets during UN synthesis, grinding, pressing, and sintering must be accomplished within a dry N_2 atmosphere having less than 10 ppm O_2.

Process requirements for grinding, blending, and granulation are defined by the process bounds investigated by Matthews, et.al[8]. A conventional vibratory ball mill fulfills this requirement. The reactive nature of UN in air requires that these operations be performed in a dry N_2 atmosphere. Placing the ball mill in the N_2 atmosphere requires that the mill motor and switches be designed to operate under those conditions. Powder grinding and blending capability is enhanced with the ability to pass a reactive process gas (N_2, H_2/N_2 mixture) or inert flush gas (Ar, He) through the milling jar during the milling process[12,13]. This capability is included as a process requirement.

The pressing of green uranium nitride pellets that sinter to target densities has been demonstrated at pressures of 50 ksi[7]. Again, due to the reactivity of UN with air, pressing must take place in a dry N_2 atmosphere. The published literature[7,8,9,10] demonstrates that UN can be sintered to greater than 90% full theoretical density at process temperatures of 1650 C within 12 hours sintering time. UN can optionally be sintered in N_2 atmosphere to correct for hypo-stiochiometry or Ar atmosphere to eliminate excess N_2 and avoid formation of sesquinitride and resultant cracking.

However, the sintering requirements that dictate that the sintering furnace be operated at 1650 $^{\circ}$C. also sets performance requirements on the $MoSi_2$ heater elements. The furnace heater elements must operate in air to maintain required maximum performance.

Based on this background, the process diagram integrating the requirements for synthesis, grinding, pressing, and sintering was developed for the initial test plan implementation (shown in Figure 1). The diagram was developed to provide a primary tool for assessing the requirements and defining specifications for laboratory scale production and to define analytical capabilities needed to support the nitride based fuel development. The diagram in general identifies process mixtures and conditions within each process operation. The furnace process operations (blue boxes) do not define a time-based sequence of process steps. The furnace operations do define process changes and process effluents resulting from these changes.

Figure 1. UN Pellet Fabrication Process Diagram (Initial Test Plan)
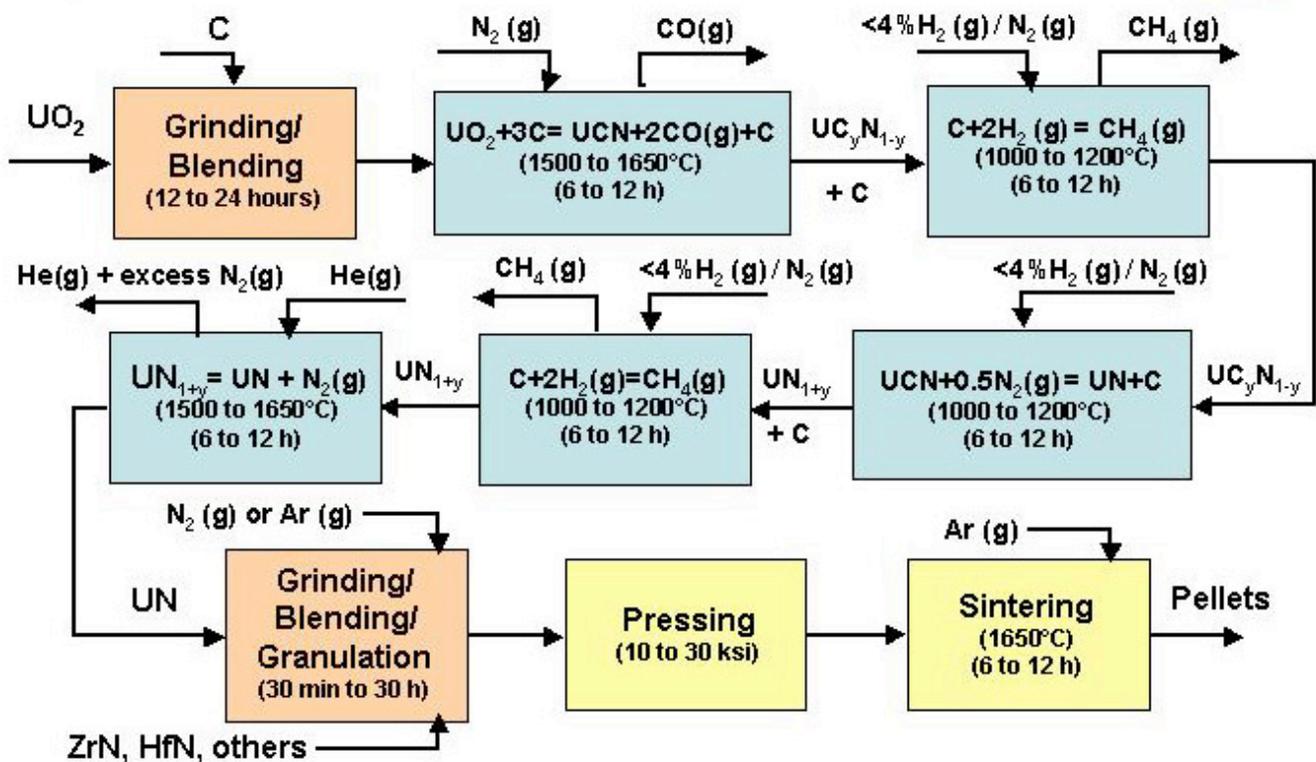
The process diagram also indicates the need to control quality and purity of materials (process inputs). As an example, UO_2 oxidizes when stored in air. The lattice parameter for uranium oxide (fluorite lattice structure) decreases with increased oxygen content[11]. X-ray diffraction (XRD) of as-received UO_2 can indicate hyper-stoichiometry as high as $UO_{2.18}$. Therefore, the as-received uranium oxide should be furnace reduced back to near-stoichiometry and verified by XRD, to minimize this source of excess oxygen. Likewise, the carbon is certified to 99.999% purity to minimize other process contamination, and all process gases are certified for purity.

Facility Specifications

The preceding process requirements translate into specifications for hardware performance requirements and analytical capabilities to support nitride based fuel development. These are as follows:

Grinding/Blending (in glove box):
   Dry clean N_2 atmosphere
   Reactive gas ball milling (N_2, H_2/N_2, He)
   Process gas analysis capability

Furnace processes/Sintering (not in glovebox):
   Sealed furnace tube (N_2, H_2/N_2, He, Ar)
   Air atmosphere for heater elements ($MoSi_2$)
   Controlled process flow rate (N_2, H_2/N_2, He, Ar)
   Programmed operation to 1650C for 30+ hrs
   Logged furnace temperature data
   Process gas analysis capability

Glove box:
   Dry, clean N_2 atmosphere (less than 10 ppm O_2)
   Oxygen monitor to verify box atmosphere
   Purged (dry N_2) large volume load chamber
   Low heat load (furnace outside of glovebox)
   Precision balance, press, disassembly area

Press (in glove box):
   50 ksi green compacting die pressure
   Dry, clean N_2 atmosphere (less than 10 ppm O_2)

Material certification:
   Verification of process material quality
   Certification of process gas sources

Gas analysis:
   Gas mass spectrometry
   Logged process monitoring

Sample analysis:
   X-ray diffraction to identify phases

Photospectrometry for N_2, O_2, C content
Pycnometry
Ceramography
Scanning electron microscopy
Support laboratories

Facility Implementation

The facilities to support nitride fuel development are implemented within three primary facility components: glove box, furnace hood, and analysis capabilities (gas analysis cart, distributed data collection, analytical support labs) shown in Figure 2.

Figure 2. Nitride facilities: glovebox (foreground), furnace hood (background), and gas analysis cart (right). Note: HEPA filtered exhaust.
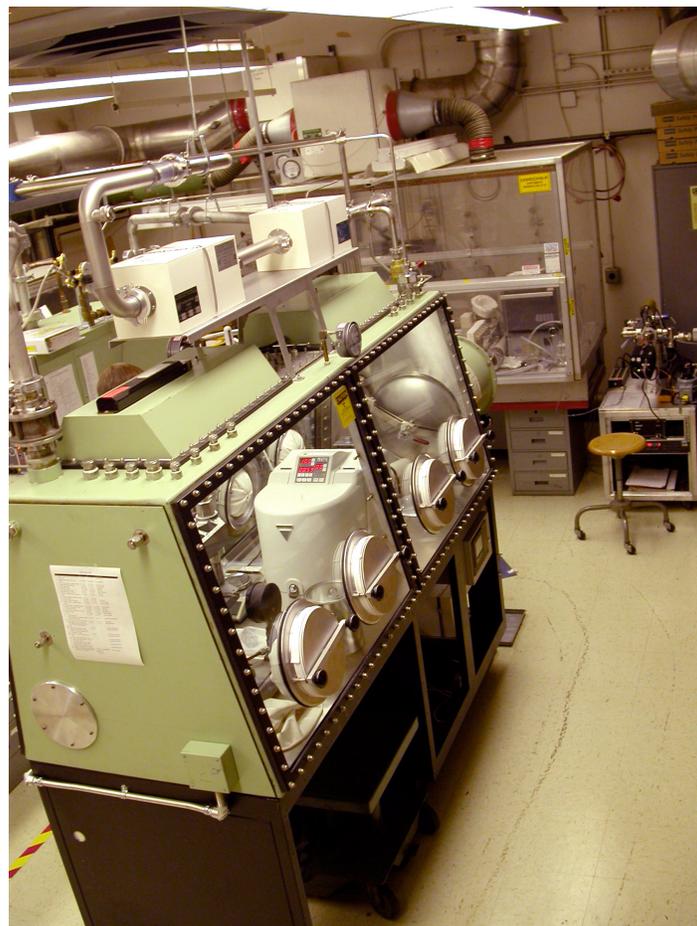
The glove box provides the capacity for locating all of the non-furnace operations within one dry, clean N_2 atmosphere. It consists of the glove box enclosure, a Dri-train catalytic bed and

molecular sieve, and a clean N_2 source. The glove box N_2 atmosphere circulates through the VAC dual bed Dri-train shown in Figure 3, which removes both oxygen and water contaminants.

Figure 3.   Dri-train catalytic bed and molecular sieve
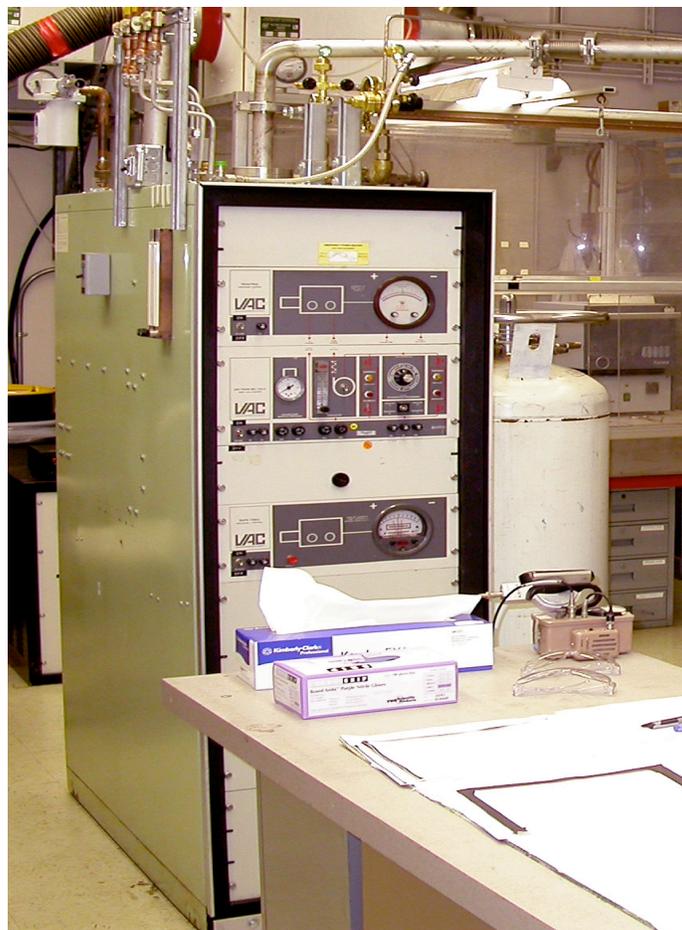
A DeltaF process oxygen analyzer installed on the glove box provides continuous glove box oxygen level monitoring. The glove box and Dri-train typically indicate oxygen levels less than 5 ppm and can operate for two weeks between Dri-train bed regenerations. The dual bed configuration allows one bed to be regenerated while the other remains in service.

The glove box contains: a 24,000 lb. Carver hydraulic laboratory press, a Fritch "pulverisette 6" planetary ball mill w/ purge gas capability, certified balance, and workspace to perform furnace tube handling operations (Figure 4).

Figure 4. Fritch mill with Carver press in foreground

The glove box is equipped with the air-lock shown in Figure 5. The port is can be evacuated to the millitorr pressure range and backfilled with N_2, or purged with N_2 until the air in the lock is diluted to ppm O_2 levels. The air-lock provides capability to move the sealed furnace tube from glove box to furnace.

Figure 5. Glove box air lock port with N_2 dewar in foreground

Figure 6. Unsealed furnace tube in glove box
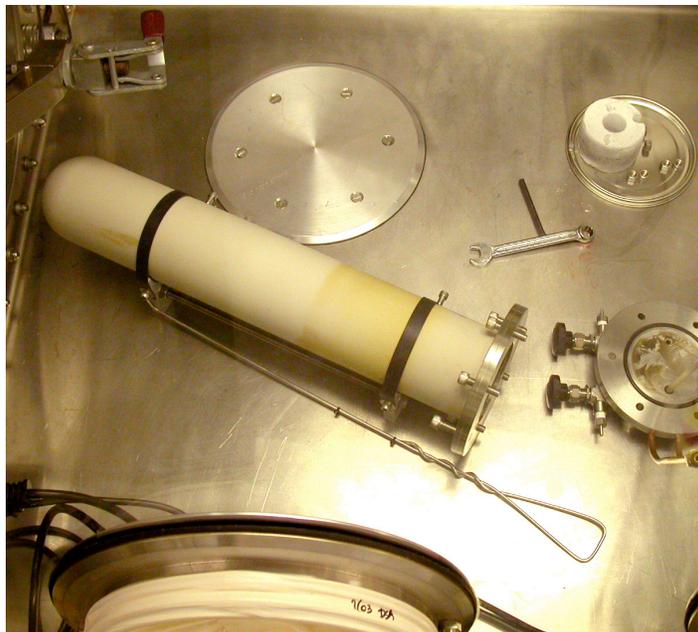
The furnace is located within the furnace hood positioned across from the air-lock port entry to the glove box. The sealed furnace tube moves between glove box and furnace hood during normal operations. The tube is handled only when at room temperature.

Figure 7. Schematic of sealed tube in furnace
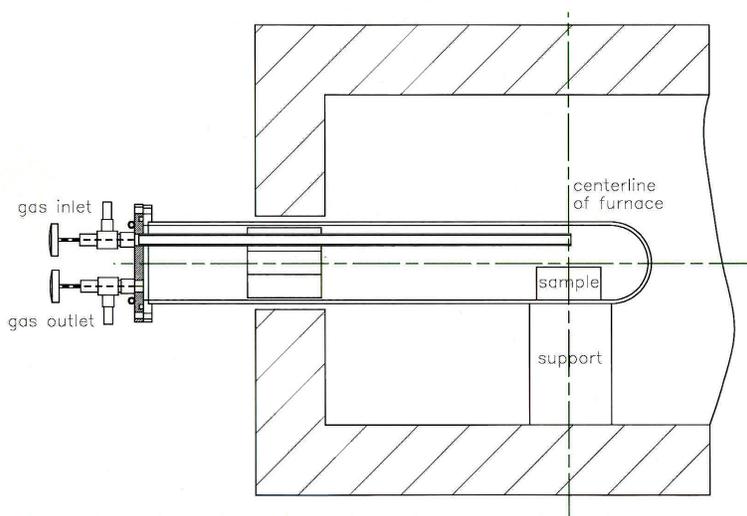
During furnace operation, purge gas from the gas outlet is configured to prevent backflow infiltration. This gas flow is continuously sampled and analyzed using an Inficon Transpector Residual Gas Analyzer (RGA) during furnace operation. Mass distribution of gas species and furnace

temperature are continuously logged using Labview and vendor software. The RGA cart also monitors purge gas from the outlet of the Fritsch ball mill during reactive milling.

Test plan implementation

The test plan for UN fuel pellet manufacturing was implemented based on the process diagram shown in figure 1. However, the initial test results did not agree with process flow diagram projections. Analysis of synthesized UN powder performed by W. Siekhaus and C. Saw on 12/04/03 indicated the constituents reacted only partially. Analysis of gas species present during processing, shown in Figure 8, indicated appropriate ratios of process gas products. Given the imposed constraints on furnace temperature (< 1650 ^{o}C) and on H_2 fraction (< 3.0 vol %) allowed in the process gas mixture, the process duration was increased to allow sufficient H_2 and time for mixture to react. An approximate molar balance of reactants and products, assuming ideal efficiencies and using actual batch sizes and process gas utilization, suggests that less than 10% of the fed N_2/2.9vol%H_2 mixed process gas was available to react and produce nitride.

Process durations were eventually increased to those shown in Figure 9. The resulting product is predominantly but not entirely UN, as indicated by the larger nitride peaks shown in Figure 10. A corresponding Reitveld refinement analysis assesses the ratio of UN:UO_2 at roughly 10:1, with other minor peaks not identified.

Figure 8.   Real time process gas analysis

Run UN_082803 - UO_2+3C+N_2 = UCN+2CO(g)+C
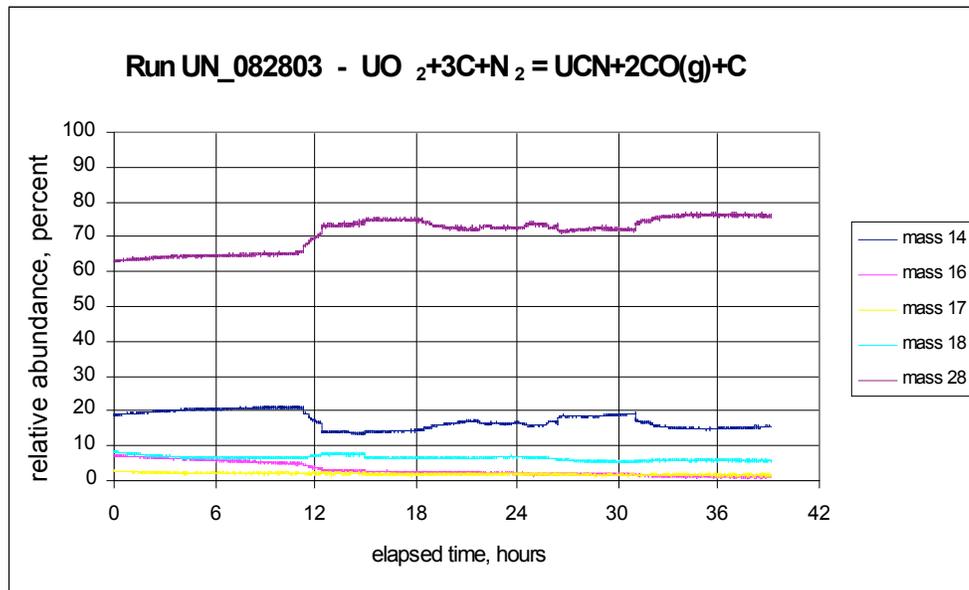
Figure 9.   UN process flow diagram (evolved final test plan)

C

N₂ (g) → CO(g)

<4%H₂ (g) / N₂ (g)

CH₄ (g)

UO₂ → **Grinding/ Blending** (12 to 24 h) → **UO₂+3C= UCN+2CO(g)+C** (1500° C) **(100 hours)** → UC_yN_{1-y} + C → **C+2H₂ (g) = CH₄ (g)** (1300° C)

Ar(g)

CH₄ (g)

<4%H₂ (g) / N₂ (g)

<4%H₂ (g) / N₂ (g)

UN₁₊ᵧ= UN + N₂(g) (1300° C) **(75 hours)** ← UN_{1+y} ← **C+2H₂(g)=CH₄(g)** (1300° C) ← UN_{1+y} ← **UCN+0.5N₂(g) = UN+C** (1300° C) **(75 hours total)** + C ← UC_yN_{1-y}

N₂ (g) or Ar (g)

Ar (g)

UN → **Grinding/ Blending/ Granulation** (30 min to 30 h) → **Pressing** 10 to 30 ksi → **Sintering** (1650° C) (6 to 12 h) → Pellets

ZrN, HfN, others →
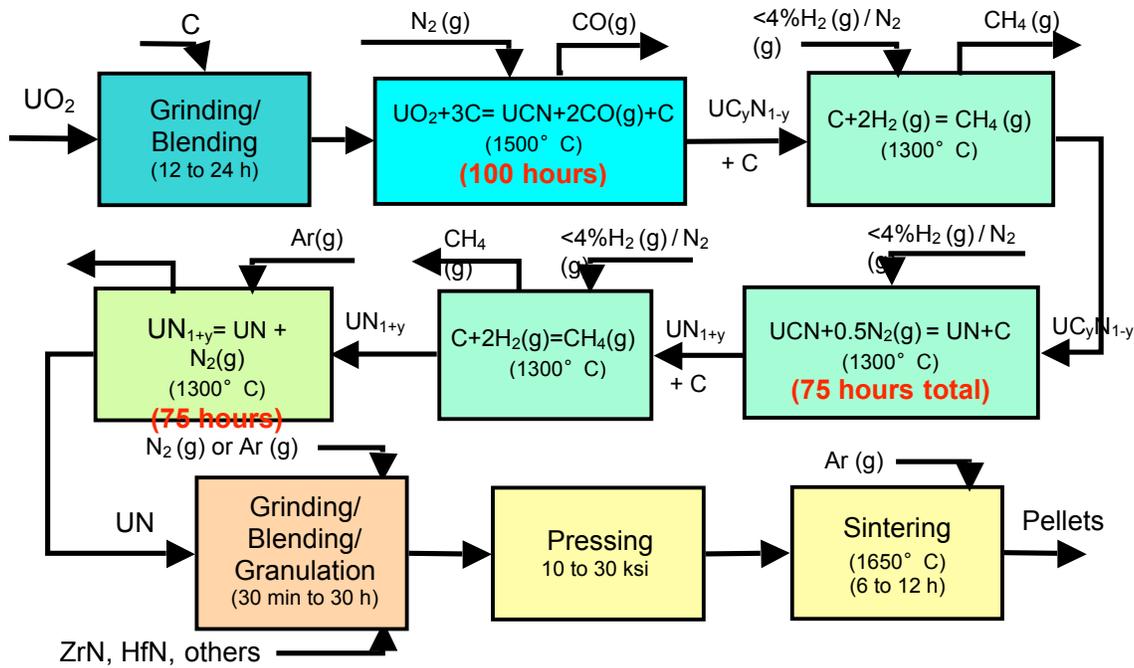
Figure 10. X-ray diffraction spectra (per C. Saw)

X2624A

counts

2theta

Uraninite-C
P41-1422
UO2 Black

Uranium Nitride
P32-1397
UN Darkgray

Uranium Oxide
P17-0659
UO

Facility Operation
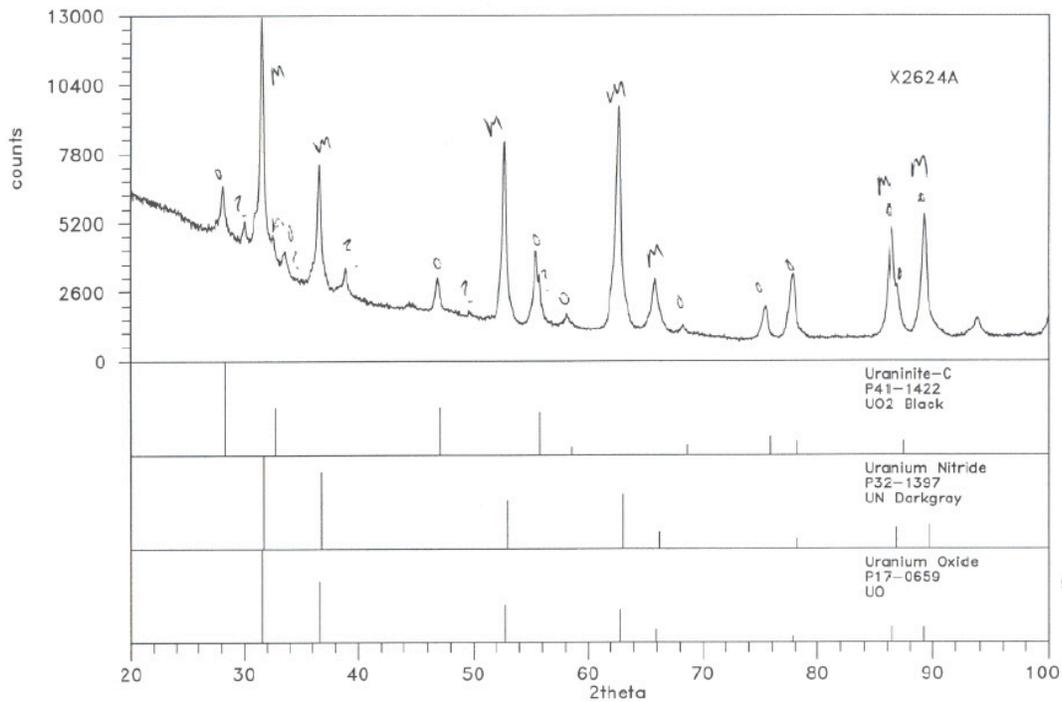
The reactive nature of UN in air required that operations be performed in a dry N_2 atmosphere. The ball mill was located in an N_2 atmosphere glove box, requiring the mill motor and switches be designed to operate under those conditions. The installed Frisch ball mill met all process requirements and preformed to specification.

The pressing of green uranium nitride pellets was performed at pressures of 5-8 ksi, much lower than the referenced pressures of up to 50 ksi   Use of higher pressures was found to produce transverse cracking in the green pellets, the result of residual tensile stresses in the pellet after release of pressing load.   Again, due to the reactivity of UN with O_2, pressing was performed in the dry N_2 glove box. The installed Carver press met all process requirements and performed to specification.

The published literature[7,8,9,10] suggesting that UN could be processed and sintered at temperatures of 1650°C and the realities of budget led the project team toward the decision to modify an existing tube furnace for UN processing and sintering. The existing furnace was required to be placed in an air hood to allow operation at its maximum operating temperature limit of 1650°C, determined by the requirement that its $MoSi_2$ heater elements operate in air. Operation of the heater elements in N_2 derated the maximum furnace temperature to 1400°C, eliminating this option. More recent literature[7] suggests that UN should be processed at temperatures of 1800°C using N_2/8vol%H_2 mixed process gas , resulting in a nominally 85% dense product with residual carbon content on the order of 1500 ppm.

Although this tube furnace performed reasonably given its limitations, it allowed only a very small batch sizes, facilitated inefficient usage of process gas, was tedious to load and unload, and was prone to outages caused by material failures during operation at maximum temperatures for extended periods of time. Furnace outages generally resulted in loss of the test sample batch.   The furnace was ultimately temperature and batch size limited; investigating higher operating temperatures and utilizing larger batch sizes would have been highly desirable during processing and sintering tests.

A new furnace, implementing these needed capabilities, was defined in a proposal for work with a consortium of nuclear fuel research institutions following completion of this LDRD. Site preparations for the new furnace were completed using additional funding provided under the LDRD for this purpose. This effort involved removing the existing furnace and furnace air enclosure and relocating the HEPA filters that were part of the air enclosure. Completion of this work is shown in Figures 11a and 11b.

The VAC glove box and dri-train installation that was completed during the first year of this LDRD (FY03) provided the key capability needed for the handling of the nitride powder during processing. The glove box performed to specification and met all processing requirements. This installation, using N_2 process gas from an LN dewar to replenish the glove box atmosphere and flush the furnace, provided approximately 2 weeks supply between changes and was vital in maintaining the N_2 glove box atmosphere at O_2 levels less than 10 ppm.

Figures 11a and 11b – Site of furnace air enclosure and same site following enclosure removal and relocation of HEPA filters for furnace upgrade

Test Result Summary

The first year of this project, from October 2002 through September 2003, focused on process design, facility upgrades, and new equipment activation. During this first year, the tube furnace was modified to meet project requirements, the glove box was procured and installed, the ball mill and press were procured and placed in the glove box, and all equipment was activated and verified as operating within the specifications of the initial test plan, prior to start of process tests. Once the facility was fully activated, a total of twenty one uranium nitride tests, shown in Table 1, were completed from October 2003 through August 2005. The remaining two months of FY05 were spent in removing the furnace air enclosure and relocating HEPA filter hardware in preparation for the facility furnace upgrade.

A chronological review of the Table 1 test results provides some insight as to problems encountered and the resulting evolution of the test plan. After the 12/04/03 test, it became apparent that longer furnace runs would be needed due to furnace temperature limitations and processing inefficiencies and that furnace operating time between failures was going to be an issue. A series of platinum-rhodium thermocouple failures, caused by material loss at the thermocouple juncture and resulting in immediate furnace outage, were attributed to reaction with the furnace reducing gas environment. A fully sheathed replacement thermocouple was identified and implemented. The sheathed thermocouple completely eliminated this mode of furnace failure.

Table 1. Summary of LDRD uranium nitride processing tests.

run ID	sample number	green material density (g/cm³)	green material mass (grams)	sintered material mass (grams)	sintered material density (g/cm³)	comments
10_20_03	powder batch	N/A	N/A	N/A	N/A	furnace outage, TC failure (24 hour duration test)
12_04_03	powder batch	N/A	N/A	N/A	N/A	(24 hour duration test)
01_27_04	powder batch	N/A	N/A	N/A	N/A	UO2 reduction (12 hour duration test)
03_01_04	powder batch	N/A	N/A	N/A	N/A	furnace tube cracked (84 hour duration test)
04_26_04	pellet batch	N/A	N/A	N/A	N/A	TC failure (72 hour duration test)
05_10_04	pellet batch	N/A	N/A	N/A	N/A	TC failure, sheathed TC's ordered
05_24_04	1	N/A	2.0	1.754	N/A	pellets soft and easily friable
	2	N/A	2.0	1.736	N/A	
06_14_04	1	N/A	2.0	1.767	N/A	pellets slightly harder but still very friable
	2	N/A	2.0	1.780	N/A	
	3	N/A	2.0	1.747	N/A	
07_27_04	1	N/A	3.000	2.848	5.92	green mixture 11.3 wt% carbon
	2	N/A	3.000	2.916	6.04	(190 hour duration test)
	3	N/A	2.695	2.626	5.95	
08_04_04	1	N/A	3.000	N/A	N/A	furnace tube cracked
	2	N/A	3.000	N/A	N/A	(furnace outage after 20 hours into test)
	3	N/A	3.000	N/A	N/A	
	4	N/A	3.000	N/A	N/A	
09_28_04	1	N/A	3.000	N/A	N/A	material reused from 08_04_04 test
	2	N/A	3.000	N/A	N/A	all pellets were cracked and rejected
	3	N/A	3.000	N/A	N/A	(190 hour duration test)
	4	N/A	3.000	N/A	N/A	
10_25_04	1	5.027	2.000	1.651	5.517	repeated green mixture 11.3 wt% carbon
	2	5.073	2.001	1.690	5.443	(190 hour duration test)
	3	5.053	1.993	1.665	5.869	
	4	5.022	1.998	1.661	5.722	
	5	5.068	1.999	1.645	5.854	
	6	5.096	1.993	1.669	5.854	
11_05_04	1	4.727	2.246	1.852	4.018	green mixture 15.0 wt% carbon
	2	4.698	2.249	1.808	3.701	pellet 2 very friable
	3	4.685	2.243	1.821	3.734	furnace tube cracked, pellets salvaged
	4	4.718	2.243	1.825	3.916	(190 hour duration test)
	5	4.756	2.245	1.839	4.031	
	6	4.700	2.250	1.838	3.746	
11_17_04	2	N/A	1.794	1.780	N/A	pellets 2 and 6 re crushed and pressed
	6	N/A	1.794	1.532	N/A	(190 hour duration test) pellets rejected
01_31_05	1	4.741	1.982	1.842	6.189	green mixture 8.7 wt% carbon
	2	4.858	1.990	1.802	5.786	(190 hour duration test)
	3	4.934	1.996	1.818	5.837	
	4	4.841	1.991	1.821	5.873	
	5	4.772	1.995	1.834	6.162	
	6	4.953	1.987	N/A	N/A	pellet 6 fractured
03_10_05	1	4.423	1.998	1.822	6.565	increased green mixture to 9.1 wt% carbon
	2	4.417	2.003	1.826	6.267	(242 hour duration test)
	3	4.438	2.005	1.827	6.387	
	4	4.423	1.998	1.816	6.191	
	5	4.445	2.005	1.827	6.812	
	6	4.439	1.995	1.823	6.568	

run ID	sample number	green material density (g/cm^3)	mass (grams)	sintered material mass (grams)	density (g/cm^3)	comments
03_29_05	1	4.393	1.992	N/A	N/A	repeated green mixture at 9.1 wt% carbon
	2	4.413	2.001	N/A	N/A	(242 hour duration test)
	3	4.396	2.001	N/A	N/A	
	4	4.427	2.000	N/A	N/A	furnace tube failed during cooling
	5	4.444	2.000	N/A	N/A	all pellets rejected
	6	4.357	1.660	N/A	N/A	
04_18_05	1	4.423	1.998	1.811	6.055	repeated green mixture at 9.1 wt% carbon
	2	4.490	1.998	1.807	6.127	(242 hour duration test)
	3	4.431	2.002	1.797	6.394	
	4	4.463	2.001	1.802	6.585	
	5	4.460	2.000	1.807	N/A	pellet 5 cracked across diameter
	6	4.463	2.001	1.816	6.454	
05_13_05	1	6.055	1.881	1.827	6.588	pellets 1, 2, and 3 from 04_18_05 test
	2	6.127	1.807	1.829	6.622	
	3	6.394	1.797	1.824	6.391	
	4	5.498	2.002	2.076	7.460	pellets 3, 4, and 5 are 75wt% HfN - 25wt% UN
	5	5.515	2.008	2.067	7.428	pellets 3, 4, and 5 gained mass
	6	5.544	2.000	2.057	7.814	
06_23_05	1	4.667	2.014	1.831	6.591	repeated green mixture at 9.1 wt% carbon
	2	4.703	1.998	1.820	6.610	(256 hour test duration)
	3	4.554	1.996	1.821	6.587	pellet 3 fractured
	4	4.664	1.997	1.822	6.867	small furnace tube crack at end of test
	5	4.635	2.000	1.824	6.969	
	6	4.615	2.007	1.831	6.866	
08_01_05	1	4.672	2.016	1.842	6.189	repeated green mixture at 9.1 wt% carbon
	2	4.655	1.993	1.802	5.786	(256 hour test duration)
	3	4.685	2.006	1.818	5.837	
	4	4.729	2.009	1.821	5.873	
	5	4.686	2.022	1.834	6.162	
	6	4.708	1.000	0.910	6.860	

The other mode of furnace failure, tube cracking, was minimized but not fully eliminated through use of gradual thermal ramping (1.5 $^\circ$C per minute), careful use of thermal insulation to maintain an acceptable thermal gradient on the tube, and frequent furnace tube replacement. Furnace tube failure usually resulted in leakage of air into the furnace tube, converting of all nitride back to oxide.

Once these issues were managed, run durations were increased with the intent to fully react process constituents, determine the "end of test" sample composition, and adjust initial C fraction to minimize excess UO_2 or C remnants. The goal of fully reacting all batch constituents was approached but not verified. Furnace temperature and fraction H_2 process gas mixture limitations were adverse to achieving this result. The low sintered density of the "end of test" material, with respect to full theoretical density, suggests that full reaction of constituents was not achieved, even with run durations in excess of 250 hours. Working within this limitation, the C fraction in the initial C/UO_2 mixture was iterated toward an optimum of 9.1 wt%. But without confidence that the materials were fully reacted, this is only an approximation of the optimal mixture.

The mixture of HfN and UN, in a mass ratio of 3:1, produced hard sintered pellets that were also significantly less dense than full theoretical density.

The slightly increased density of UN test pellets that were resintered strongly suggests that higher sintering temperatures were needed, consistent with the observations of Rogozkin, et.al.[14]

Finally, none of the test pellets were of sufficient purity to permit thermal conductivity measurement within the instrument measurement range, defined by the thermal conductivity of uranium nitride, nominally 15 W/m-$^{\circ}$K at room temperature.

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5.   ANALYSIS OF MONO-URANIUM NITRIDE FUEL PERFORMANCE

The current capability for analysis of mono-uranium nitride fuel performance is based on the semi-empirical computer code, SPACEPIN[1]. The SPACEPIN code was developed as a subroutine for the SP-100 COROPT-S[2] code, which analyzes the integrated performance of the reactor and interfacing subsystems of the total space reactor system. SPACEPIN, which can also be used as a stand-alone code, includes routines for design analysis, and also special purpose features for analysis of irradiation tests of pressurized tube specimens, irradiations in thermal and fast reactors.

The SPACEPIN temperature, fuel swelling, fission gas release, cladding deformation, and nitrogen transport models are described below. The fuel pellet column in SPACEPIN is divided into 10 equal-length axial segments. Power, coolant, and flux conditions are assumed steady over each time step. The fuel is centered in the cladding. Heat transfer is radial. Calculations are made at the axial center of each segment. Fission gas released is accumulated over the axial segments to calculate the fuel pellet internal pressure.

Temperature

The SPACEPIN thermal model uses established fuel pellet thermal analysis methods to calculate the temperature distribution from the cladding outer surface temperature radially through the cladding/liner, across the gap between the cladding/liner and the fuel pellet, and to the fuel pellet center.

The cladding outer diameter and outer surface temperature are input at the beginning of the time step. The temperature rise through the cladding and liner tubes is calculated by the following equation:

$$\delta T \; = \; (q \,/\, l)/2\pi k \; \text{x} \; \ln (D_o \,/\, D_i)$$

where δT = Temperature rise
$(q \,/\, l)$ = Linear power
k = Cladding/liner thermal conductivity
D_o = Outer diameter
D_i = Inner diameter

The Ross-Stoute formulation is used to calculate the gap conductivity. This formation accounts for the three modes of heat transfer across the gap: conduction through the gas, radiation across the gap, and solid-to-solid conduction. The gap conductivity changes with exposure due to the increasing concentration of fission gases in the he fill gas, and the closing of the gap as the fuel swell.

The thermal modeling of the UN fuel pellet at the low linear power typical of space reactor applications is straightforward compared to an oxide fuel pellet. The temperature gradient through the pellet is small, due to the high thermal conductivity of UN. With these small gradients, restructuring of the fuel, formation of a central void, and cracking due to thermal stresses do not occur. The solid fuel pellet remains a solid cylinder, as shown in Figure 1 after 6 atom% of burnup. The fuel temperature distribution is calculated used the integral kdt method.

Figure 1. SP-100 UN at 6 at. % Burn-Up
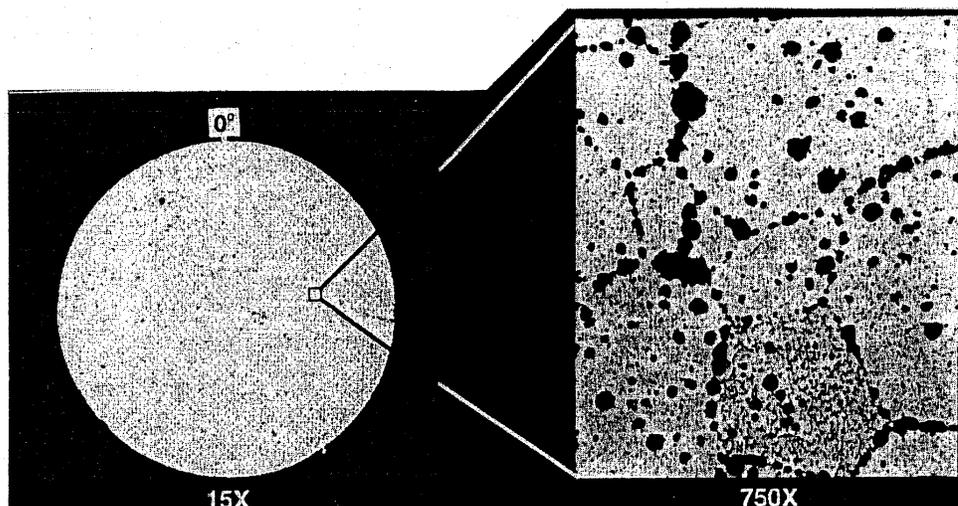
Fuel Structure in High Burnup (6 atom percent) High Density UN Fuel Showing Porosity at Grain Boundaries (SP3RR Test).

$$\int k\,(T)\,dT \quad = \quad (q/l)/4\pi \ \times \ (r_o^2 - r^2)/r_o^2$$

where T	=	Temperature
k (T)	=	Fuel thermal conductivity
$\int$ k (T) dT	=	Integral from temperature at fuel surface to temperature at radius r
(q / l)	=	Linear power
r_o	=	Fuel pellet outer radius

Fuel Swelling

The fuel pellet is fabricated with a gap between the fuel pellet and the inner surface of the cladding/liner. Swelling of the fuel can close this gap. After gap closure, the swelling fuel produces a secondary load at the inner surface of the cladding/liner, contributing to the increase in fuel pellet diameter over lifetime.

The growth of the fuel pellet during irradiation is caused by the accumulation of solid and gaseous fission products within the fuel lattice. The SPACEPIN fuel swelling model accounts for the known phenomena of solid fission product swelling and temperature dependent enhanced swelling due to gas bubble formation. Below a temperature threshold, UN swells due only to the accumulation of fission products in the fuel lattice, and is independent of temperature and solely a function of burnup. Above the temperature threshold, fission gas bubbles form and swelling becomes burnup and temperature dependent. The SPACEPIN fuel swelling model uses the Zimmerman formulation developed for carbide fuel.

$$X \quad = \quad \alpha \ + \ \beta \, / \, \{1 \ + \ e^{\,[(\gamma \, - \, T) \, / \, \delta]}\}$$

$$Y \quad = \quad \tau \ + \ \mu \, e^{\,(- \, Q \, / \, RT)}$$

$$S \quad = \quad \sigma \, B \ + \ X \, [\, 1 - e^{(-YB)}]$$

Where   T   =   Fuel temperature (volume average)
         R   =   Gas constant
         B   =   Burnup
         S   =   Fuel volume change
and α, β, γ, δ, τ, μ, σ, and Q are coefficients.

In the SPACEPIN model, UN swelling isotropically until gap closure, and anisotropically after gap closure at a fixed diameter/axial swelling ratio. The model compressive creep (hot pressing) of the UN fuel pellet as a mechanism for accommodating fuel swelling after gap closure.

Fission Gas Release

Gaseous fission products generated within the fuel lattice can be released from the fuel pellet into the void spaces within the fuel pellet. The released gas increase the fuel pellet internal gas pressure. The gas pressure produces a primary load at the inside surface of the cladding/liner, contributing to the increase in fuel pellet diameter over lifetime.

The SPACEPIN fission gas release model[3] is a material balance formulation that takes into account the following observations of fission gas behavior in UN fuel pellets at space reactor operating conditions:

- Fission gas atoms move within the grain matrix by single atom diffusion,
- The atoms either form bubbles within the matrix or at the grain boundary,
- Intragranular bubbles are stationary in the small temperature gradient,
- The intragranular bubbles trap gas atoms,
- The release mechanism is diffusion to the grain boundary,
- As grain boundary bubbles link up, all gas reaching the boundary is released,
- The fraction of fission gas atoms generated that are released is determined by the relative rates of transport to the bubble traps within the grain matrix and the interlinked bubbles at the grain boundaries.

The rate of change in retained fission gas in the fuel pellet is derived from the balance between the rate of fission gas production and the rate of loss.

$$dC/dB \quad = \quad dG/dB - f\,C$$

where   C   =   Retained fission gas
        B   =   Burnup
        dC/dB =   Rate of change in retained fission gas
        dG/dB =   Fission gas generation rate
        f   =   Fractional release of retained fission gas

The resulting equations are:

$$\delta R \quad = \quad C_o\,[\,1 - e^{(-f\,\delta B)}\,] \; + \; (dG/dB)\,\delta B\,\{\,1 - [\,1 - e^{(-f\,\delta B)}\,(1\,/\,f\,\delta B)]$$

$$f \quad = \quad \alpha\,P^{\,\beta}\,\{\,1 - e^{[-\gamma\,P\,(dT/dr)B]}\}\;e^{\,(-Q/RT)}$$

where δR = Fission gas release increment
        C_o = Retained fission gas at the beginning of burnup increment
        δB = Burnup increment
        P = Fractional fuel porosity (as fabricated)
        T = Fuel temperature (volume average)
        dT/dr = Fuel temperature gradient
        R = Gas constant
and α, β, γ, and Q are coefficients.

The post irradiation examination of the SP-100 fuel pellets irradiated at EBR-II and FFTF indicated that the fission gas release rate varies as functions of burnup and as-fabricated UN fuel pellet densities, as shown in Figure 2[4].

Figure 2. SP-100 UN Fuel Pellet Fission Gas Release Rate
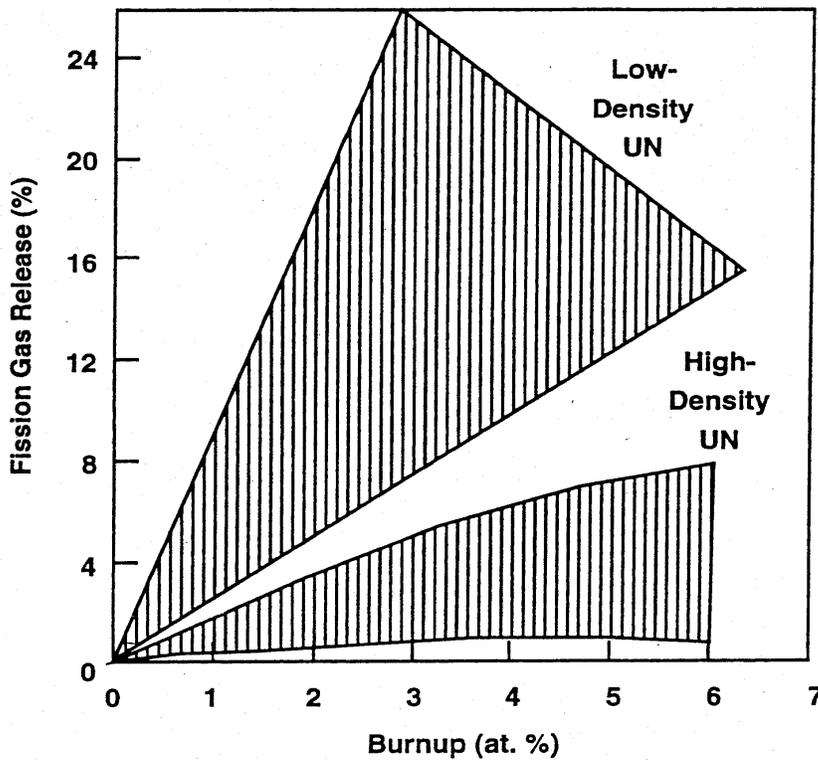
Cladding Deformation

For reactor design, the cladding diameter increase must be limited to prevent interference with the coolant flow, and for material performance the deformation must be less than the ductility limit.

The SPACEPIN structural model calculates the deformation of the bonded cladding/liner under the load produced by the internal gas pressure and the mechanical interaction with swelling UN fuel. The model includes account of the thermal expansion, elastic strain, thermal and irradiation creep, and irradiation reduced swelling of the cladding/liner materials. The diameter increase at the cladding outer surface for the operating conditions during each time step is determined by solving the stress-strain relationships for a two-material concentric tube for the boundary conditions at the bonded interface.

Nitrogen Migration

Loss of nitrogen from the UN fuel can produce liquid uranium at the fuel pellet surface. The liquid uranium can react with the inner surface of the liner, reducing its effective thickness. The nitrogen loss from the fuel is controlled by the nitrogen partial pressure in the fuel pellet. The nitrogen loss from the fuel is minimized by maintaining the nitrogen partial pressure by minimizing nitrogen loss from the fuel pellet.

In the as-fabricated fuel pellet, the nitrogen distribution is uniform. As the reactor rises to operating temperature, nitrogen is released from the fuel surface into the void spaces of the fuel pellet. Nitrogen from within the fuel diffuses to the surface under the nitrogen concentration gradient until a quasi-equilibrium is reached between the fuel concentration at the pellet surface and the nitrogen partial pressure in the fuel pellet. Equilibrium is not reached because nitrogen is being lost from the fuel pellet by diffusion through the liner to the cladding and by migration of the nitrogen to the exposed cladding in the end plug regions. The SPACEPIN nitrogen transport model follows the diffusion of nitrogen within the UN fuel, determines the (N + C + O)/U rationat the pellet surface and the nitrogen partial pressure in the fuel pellet, and then follows the diffusion of nitrogen through the liner and the migration of nitrogen to the end plug regions.

In the SPACEPIN model, the cladding is effectively an infinite sink for nitrogen. The nitrogen is assumed to first react with the zirconium. After the Zr is depleted, the nitrogen is assumed to dissolve in the niobium up to the solubility limit. After the solubility limit is reached, Nb nitride id assumed to form at the inside surface. Diffusion of nitrogen in the Nb-1%Zr cladding axially down the concentration gradient from the end plug regions, and nitrogen diffusion from the Nb-1%Zr into the coolant, are not taken into account.

The SPACEPIN modeling of the nitrogen transport rates is conservative. All fuel is assumed to be at the axial peak volumetric average nodal temperature for calculating nitrogen diffusion within the pellet, all the fuel surface is assumed to be at the axial peak temperature for calculating the nitrogen partial pressure, and all the liner adjacent to the fuel column is assumed to be at the axial peak liner mid-wall temperature for calculating nitrogen diffusion through the liner. The nitrogen diffusion rate within the fuel is assumed to be constant, and dependent on the nitrogen concentrations in the surface and next interior nodes. This conservatism is not extended beyond the fuel column. The local axial average temperature is used to calculate the migration of nitrogen past the spacers or reflectors to the end plug regions. The result of these assumptions is an over-prediction of the nitrogen transport rates.

Analysis Issues

- Uncertainties in the liner-to-fuel gap conductance remain.

- The plutonium buildup in the fuel is not modeled. An increase Pu concentration reduces the UN thermal conductivity

- Fuel Thermal and irradiation creep and hot pressing of the pellet porosity, are not accounted for in the fuel swelling model.

- Fuel swelling and fission gas release are modeled as separate processes.

- The nitrogen transport model may be too conservative for use in fuel pellet design.

Code Verification and Validation

More than 50,000 uranium nitride (UN) fuel pellets were manufactured for SP-100. A total of 76 experimental fuel pellets with various cladding and liner materials were irradiated in EBR-II and FFTF, Post irradiation examinations (PIE) of these pellets were performed. Table 1 and 2 shows the SP-100 UN fuel irradiation in EBR-II and FFTF[4], respectively.

The SPACEPIN code was used to analyze the SP-100 fuel pellet irradiation. The conditions are:

UN fuel with OD of 0.3" and 11.5" long,
Fuel density of 96% theoretical density (T.D.) and U-235 of 95%,
PWC-11 clad with Re liner,
Liner heat generation rate of 154 W/cm.

Table 1. SP-100 UN Fuel Irradiation in EBR-II

Test No	No. of UN fuel pins	Fuel T.D., %	Cladding /Liner	Burn-up, atom %
SP-1	4	87	Nb-1Zr / W	~1
SP-1R	4 SP-1 pins	87	PWC-11* / W	3.9
	2	87	PWC-11 / W	3
SP-2	2	87	Mo-13Re	1.3
	2	87	PWC-11 / W	1.3
SP-3	8	96	Nb-1Zr / W	0.8
SP-3R	2 SP-1 pins	87	Nb-1Zr / W	6
	6 SP-3 pins	96	Nb-1Zr / W	3.3
SP-3RR	4 SP-3R pins	96	Nb-1Zr / W	6
	4	96	Nb-1Zr / Re	3.1

Table 2. SP-100 UN Fuel Irradiation in FFTF

Test No	No. of UN fuel pins	Fuel T.D., %	Cladding /Liner	Burn-up, atom %
FSP-1	38	Various	Nb-1Zr / various liner	2.3
FSP-1R	22 FSP-1 pins	Various	Nb-1Zr /v liner	5.6
	16	96	Nb-1Zr / Re	3.1

The burn-up profile of the SP-100 fuel pellet irradiation and the irradiated cladding strain (in %) were calculated by SPACEPIN and shown in figure 3 and 4, respectively. Results of the SPACEPIN calculations (fission gas release, etc.) indicated good agreement with SP-100 fuel pellet irradiation data. Results of the cladding strain (in %) of UN fuel irradiation calculated by SPACEPIN were compared with those calculated by others using SIEX3[5]. The comparison was shown in Figure 5.

Figure 5.   Burn-up Profile of the SP-100 Fuel Pellet, Calculated by SPACEPIN
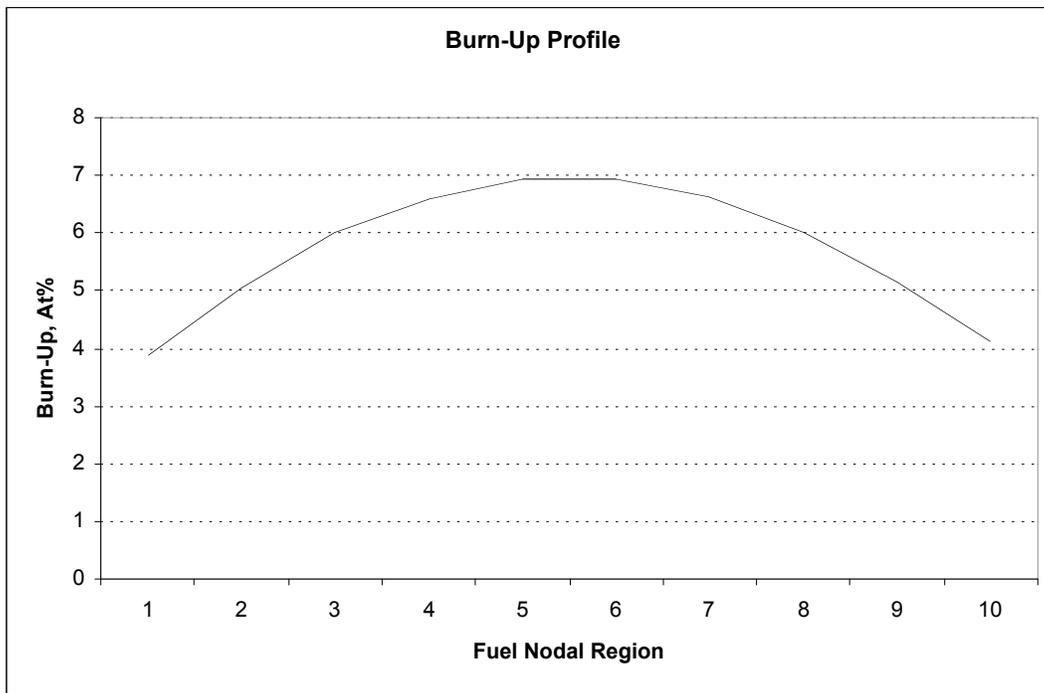
Figure 6.   Cladding Strain of UN Fuel Irradiation, Calculated by SPACEPIN

Cladding Strain of UN Fuel Irradiation

Figure 7.   Comparison of Cladding Strain of UN Fuel Irradiation Calculated by SPACEPIN and SIEX3

Peak Radial Temperature Profiles
For Mixed Nitride and Metal Fuels
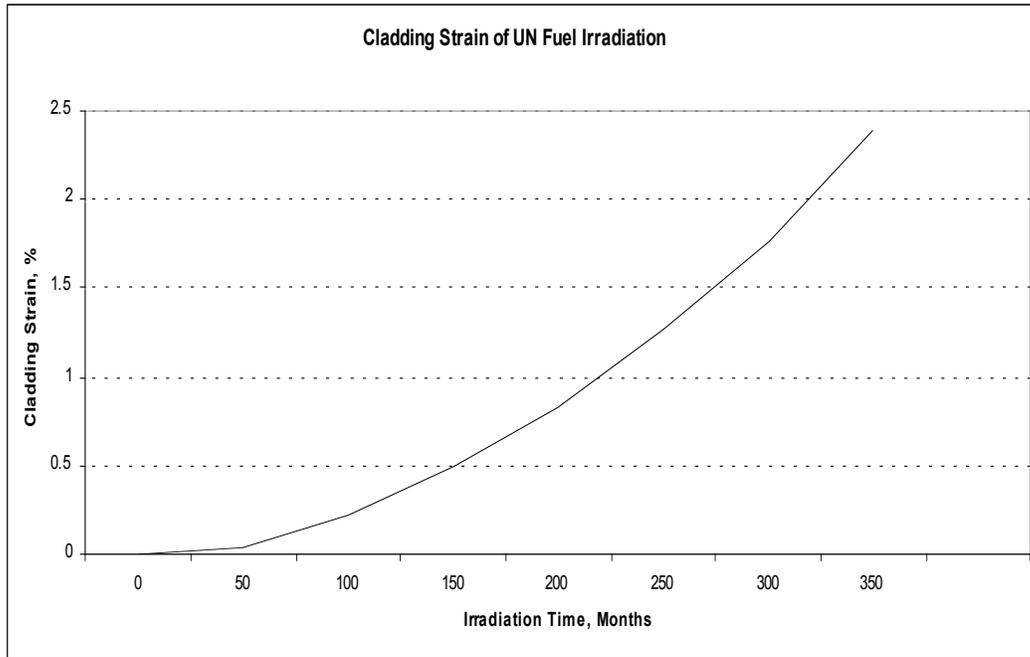
Peak Cladding Strains
For Mixed Nitride and Metal Fuels
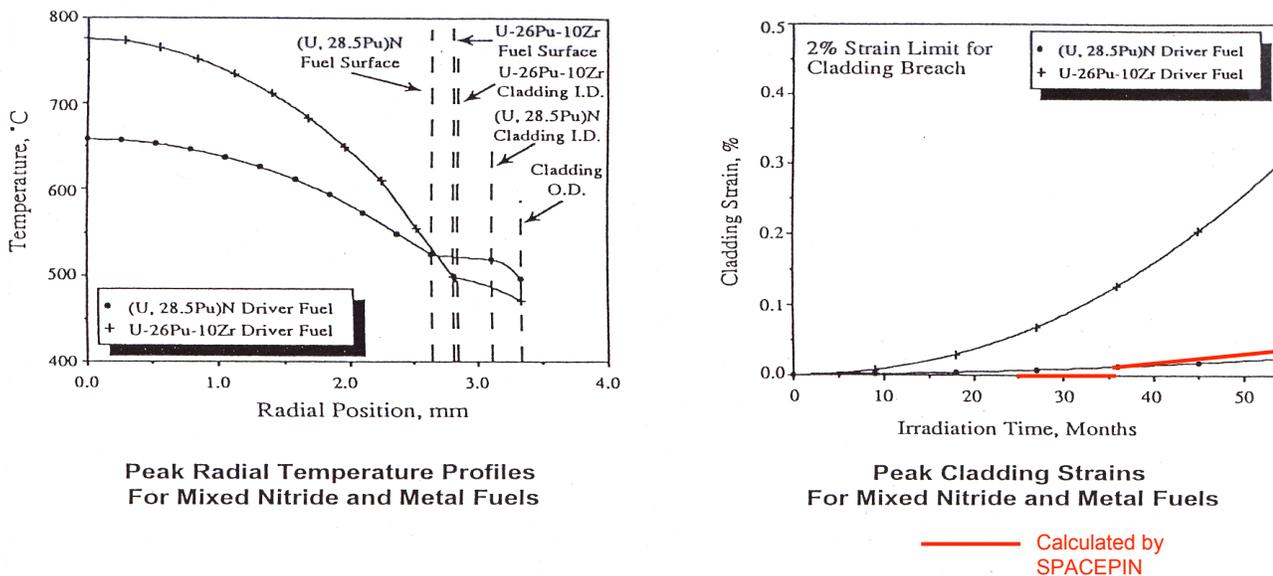
Ref.: W. F. Lyon, et.al., "Performance analysis of a mixed nitride fuel system for an advanced liquid metal reactor," ANS Meeting, November 11-15, 1990, Washington DC.

The results by SPACEPIN calculation against the PIE data from SP-100 irradiated UN pellets indicates good agreement in fission gas release, volume expansion, as well as the predication on fuel-liner gas closure and % of strain exerted on the cladding.

To enhance the computational capability in reactor code neutronic analysis, the computer code, MONTEBURNS is also acquired. MONTEBURNS consists of two codes: MCNP for particle transport calculations and ORIGEN2 for fuel depletion calculation.

The experience accumulated in using these computer codes (MONTEBURNS, MCNP, ORIGEN2, SPACEPIN, LIFE4REV1 and SIEX3) would enhance our simulation and modeling capability in reactor neutronic and fuel performance analysis.

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6.   DEVELOPMENT OF MODIFIED NITRIDE-BASED FUEL PELLETS

This LDRD project centers on the evaluation of modified uranium nitride fuels imbedded with other inert (e.g. ZrN), neutron-absorbing (e.g. HfN) , or breeding (e.g. ThN) nitrides to enhance the fuel properties to achieve long core life with a compact reactor design[1]. This study of uranium mono-nitride fuel with nitride additives was prompted by the favorable nuclear fuel properties of uranium mono-nitride (UN), i.e. high actinide density and high thermal conductivity, and the potential advantages of adding group IIIB nitrides to UN for improved fuel life.

Fuel Selection Criteria

The primary factors that affect the selection of the reactor fuel are compactness, long-life, proliferation resistance, fuel safety, and waste management. For a modified nitride-based fuel to be selected over pure uranium mono-nitride fuel, it must be superior in several of these factors and comparable in the remaining factors. The focus is on the potential benefits of adding group IIIB nitrides (*e.g.* TiN, ZrN, and/or HfN) and other actinide nitrides (ThN and/or PuN) to the base UN fuel.

1.   Compactness

Higher density of the fissionable isotope (^{235}U) favors a more compact reactor because the critical mass will be smaller. A smaller core will yield more heat per unit area and higher thermal conductivity of the fuel will be required to get the heat out of the system and maintain an acceptable centerline temperature of the fuel.

If composition of the fuel can be modified to increase the thermal conductivity without decreasing the density of the ^{235}U in the fuel or affecting the stability of the fuel, a more compact reactor design is favored. Table 1 shows the thermal conductivity of a variety of nitrides at various temperatures. The data show that additions of ThN should increase the thermal conductivity substantially. Additions of TiN or ZrN should increase the thermal conductivity slightly, and additions of HfN should decrease the thermal conductivity slightly.

Table 1. Thermal Conductivity of Various Nitrides

Material	T=20 C (W/m-K)	T=500 C (W/m-K)	T=750 C (W/m-K)	T=1000 C (W/m-K)
TiN[3]	19.2	26	27	28
ZrN[3]	20.5	23	24	25
HfN[3]	21.7	17	16	17
ThN[4]	51.5	47.7	46.0	44.8
UN[2]	14.5	20.6	22.7	24.6
PuN[19]	14.0	12.5	12.0	13.0

With the possible exception of ThN, a modified nitride-based fuel will have minimal positive or negative impact on the compactness of the reactor.   If the ^{235}U content in the fuel remains the same, the

addition of ThN could be very beneficial to the overall thermal conductivity, thus favoring a more compact design.

2.   Long-life

Long -life is obtained largely by the reactor design. But fuel composition can also affect the life favorably or unfavorably. The favorable features are:

- High fissile loading (i.e., high ^{235}U enrichment in UN, or high ^{239}Pu content in (U,Pu)N),
- Presence of ^{232}Th or ^{238}U which are converted during irradiation into ^{233}U-rich uranium and ^{239}Pu-rich plutonium, respectively,
- Low cladding strain which is dependent upon the fuel centerline temperature and the radiation effects on the fuel and cladding materials,
- Presence of burnable poisons in the fuel.

Additions of inert materials such as TiN and ZrN are a detriment to long life and only serve to dilute the active components of the fuel.

Proliferation concerns will limit the ^{235}U enrichment and cladding strain caused by radiation effects is not known for most of the nitrides under consideration in this study. Therefore, this discussion on long core life centers largely on any potential benefits that can be gained by the use of burnable neutron poisons.

Table 2 gives the neutron absorption cross sections of various elements at a neutron energy of 0.1 and 0.5 MeV. As can be seen in the table, the neutron absorption cross sections in this energy region are relatively low, even for many elements that are normally identified as good neutron poisons. Of all these elements, Eu is the best neutron poison in this energy regime, and Hf, Sm, Gd, and Dy are all considerably better than average neutron poisons.

Table 2. Neutron Absorption Cross Sections[*]

Element	Isotope	Cross Section at 0.1 MeV (barns)	Cross Section at 0.5 MeV (barns)
Ti	Nat	0.0084	0.0039
Zr	Nat	0.026	0.023
Hf	Nat	0.35	0.17
Nd	Nat	0.077	0.047
Sm	Nat	0.39	0.22
Eu	Nat	1.33	0.50
Gd	Nat	0.46	0.22
Dy	Nat	0.36	0.19
Th	232	0.26	0.18
U	235	0.42	0.17
U	238	0.17	0.11
Pu	239	0.40	0.16

The fission cross sections of some of the actinides are given in Table 3. The table shows that the fission cross section of ^{235}U and ^{239}Pu are roughly the same as Eu and about a factor of four higher than Hf, Sm, Gd, and Dy. Therefore, the rate of neutron capture by one of the burnable poisons will be a little less but still comparable to the rate of fission of the ^{235}U. Even though the neutron absorption cross sections are relatively low in this energy regime, burnable poisons could still lengthen fuel life significantly.

Table 3. Fission Cross Sections[*]

Element	Isotope	Cross Section at 0.1 MeV (barns)	Cross Section at 0.5 MeV (barns)
Th	232	0	0
U	235	1.6	1.1
U	238	0	0
Np	237	0.018	0.45
Pu	239	1.5	1.6

* Data taken from the MCNP library

3. Proliferation Resistance

Proliferation resistance is ensured primarily by the reactor design, but composition of the fuel is also a significant consideration. To ensure that the uranium in the fresh fuel is not attractive for use in nuclear weapons, the ^{235}U enrichment will be limited to 20%. The fresh fuel can be made even less attractive for diversion by the addition of other inert materials that are not readily separated from UN. Addition of inert materials that are harder than UN to dissolve in aqueous solutions enhances the proliferation resistance. Once the material is dissolved in solution, a PUREX-like purification process will provide good separation of the actinindes from the other inert materials.

Reaction or dissolution rates of nitrides are not well characterized. Table 4 summarizes available data and includes the approximate time required to completely react or dissolve the various nitride powders in water (H_2O), concentrated nitric acid (HNO_3), concentrated hydrochloric acid (HCl), and concentrated sulfuric acid (H_2SO_4). Note that water reacts with but does not dissolve ThN and PuN. Likewise concentrated nitric acid reacts with but does not dissolve TiN. All other data in Table 4 are for complete dissolution.

Overall, it is not clear that any significant benefit is obtained by adding other nitrides to the UN fuel matrix. Addition of ZrN may make dissolution in concentrated nitric acid more difficult, but it will probably make dissolution in hydrochloric and sulfuric acids easier.

Table 4. Reaction and Dissolution Properties of Powdered Nitrides in Water and Concentrated Acids

Nitride	H_2O	HNO_3	HCl	H_2SO_4
TiN	No rxn[6]	<60 m[6]	No rxn[6]	~6 d[6]
ZrN	No rxn[6]	~4 h[6]	~60 m[6]	~60 m[6]
HfN	No rxn[6]	~2 h[6]	~60m[6]	~60 m[6]
ThN	~20m[7]	No data	No data	No data
UN	No rxn[8]	~30 m[8]	No rxn[8]	No rxn[8]
PuN	~15m[9]	~90 m[9]	> 90 m & <2 d[9]	~2 d[9]

Temperature is of reaction/dissolution is approximately 95 C.

Proliferation resistance is also a consideration in the spent nuclear fuel, especially if the fuel will be reprocessed. If there is ^{232}Th or ^{238}U in the fresh fuel, the irradiation will lead to ^{233}U-rich or ^{239}Pu-rich weapons useable material in the spent fuel. The attractiveness of the Pu is reduced, but not eliminated, by the presence of higher enrichments of ^{235}U in the fresh fuel. Under irradiation, some of the ^{235}U is eventually converted into to ^{238}Pu. The attractiveness of the plutonium in the irradiated fuel is also reduced, but not eliminated, by longer irradiation times, *e.g.* higher burn-ups. The long irradiation cycle (as supported by the long life of the reactor fuel) will render the spent fuel with a higher percentage of ^{240}Pu and ^{242}Pu.

Overall, the attractiveness of the fresh fuel is reduced very little by additions of other nitrides to the UN fuel, and the attractiveness of the spent fuel is reduced some by minimizing the ^{238}U content relative to the ^{235}U content as long as the ^{235}U enrichment is kept below 20%.

4. Fuel safety

For nitride fuel and cladding, the relevant criteria for fuel safety are

- Fission gas release and retention
- Fuel pellet cladding interaction
- Radiation swelling effects
- Fuel centerline temperature

In general, the attainable burn-up and thus operating life of nuclear fuels are limited by materials performance issues, which result from changes in the thermal and mechanical properties and dimensional stability of the fuel pellets, cladding and structural materials during neutron irradiation. The development of modified nitride fuel will require improved materials and design approaches in order to reach higher burn-ups.

The effects of fission gas build-up can be mitigated by the fuel pin design. If the density of the fuel is low enough that the porosity is open, usually around 95% of theoretical or less, the fission gases will be able to diffuse out of the fuel and collect in the gaps at the ends of the fuel pins. Modification of the fuel composition is not a benefit or detriment in this respect.

The stability of the fuel with the cladding will be dependent upon the thermodynamic stability, compatibility of the materials, the fuel temperature, and radiation induced swelling effects. Thermodynamic stabilities of various nitrides are summarized in Table 5. The melting point and heat of formation are qualitative measures of the relative stability of the nitrides and show qualitatively that all the nitrides listed are more stable than UN and PuN.

Table 5. Melting Points and Oxidation Properties of Powdered Nitrides

Nitride	MP (ºC)	$\Delta_f H^0_{298}$ (kJ/mol)	Oxidation Begins (C)	Ignition Temp. in Air (C)
TiN	2945[10]	-337.6[11]	580[13]	>680[13]
ZrN	2960[10]	-365.3[11]	600[13]	>740[13]
HfN	3387[10]	-373.6[12]	650[13]	>810[13]
ThN	2827[10]	-391.2[12]	360[4]	520[4]
UN	2762[18]	-290.8[12]	100[15]	~300[15]
PuN	2469[14]	-299.2[12]	<25[9]	~290 dry[15] ~100 moist[15]

Note that MP for UN and PuN is the temperature at which they decompose into a liquid metal and 1 atm of $N_2(g)$

Also listed in Table 5 are the temperatures where oxidation of the nitride powder begins and the temperature at which the powder ignites. For bulk solids, these temperatures will of coarse be much higher. The data show clearly that additions of any of the nitrides except PuN will benefit the oxidation resistance and possibly simplify considerably the handling of the material. The best nitrides to add to the fuel matrix are clearly ZrN and HfN.

In regards to interaction with the cladding some thermodynamic calculations can be performed to see if the nitrides are stable with respect to the cladding materials, which are taken to be a zirconium-rich alloy and niobium-rich alloy. **Table 6** gives the free energy of reaction with zirconium or niobium per mole of nitride. For reaction with zirconium, the equation considered is

$$MN + Zr = ZrN + M \qquad (1)$$

And for reaction with niobium, the equation considered is

$$MN + 2Nb = Nb_2N + M \qquad (2)$$

where M is Ti, Zr, Hf, Th, U, or Pu. Thermodynamic calculations were performed using FactSage 5.0[16]. The components of stainless steels are not easily nitrided so similar reactions will not occur.

Table 6. Thermodynamic Stability of the Nitrides[16]

Nitride	$\Delta_r G^0{}_{1273}$ with Zr (kJ/mol)	$\Delta_r G^0{}_{1273}$ with Nb (kJ/mol)
TiN	-29.7	73.7
ZrN	0	103.4
HfN	12.3	115.7
ThN	18.9	122.3
UN	-56.0	47.4
PuN	-55.4	48.0

The free energy data show that UN is stabilized considerably by the addition of HfN or ThN. Without these additions, zirconium is not a suitable cladding material for uranium nitride fuel. In the case of niobium, there are no reactions with the nitrides. Consequently, no there no particular advantages or disadvantages to a modified nitride fuel when using niobium cladding. In the case of nickel, a common component of stainless steels, it is known that UN will react with nickel to form UNi_5 and U_3N_4[17]. It is not known whether or not similar reactions occur with the other nitrides or if iron or other components in stainless steels will undergo similar reactions. Further study is needed to determine whether or not there are any advantages or disadvantages when using stainless steel cladding with a modified nitride fuel.

In summary, additions of HfN and ThN and to some extent ZrN make the fuel considerably less reactive with the cladding and significantly safer to handle in an air atmosphere.

5.   Waste Management

Waste management is a complicated issue with spent nuclear fuel. If the fuel is to be used in a once through cycle and disposed of directly, it will be important that the fuel is stable for thousands of years in an underground repository. If the fuel is to be used in a close cycle, it will be important that the fuel can be easily purified and reused.

For an open once through fuel cycle, the spent fuel will eventually need to be disposed of in an underground repository. Since the components in the fuel will not be reused, it is best from a proliferation point of view to dispose of the fuel directly and not separate the fission products from the actinides thus making them attractive for theft or diversion. Nitrides are more reactive than oxides so the case for direct disposal may be more difficult. As already noted, addition of nitrides except PuN to the UN fuel will significantly stabilize the fuel making it more stable with respect to water and more resistant to oxidation. Thus, it is a significant advantage from the waste management point of view for a direct disposal option to add TiN, ZrN, HfN, or ThN to the UN fuel.

For a closed fuel cycle involving reprocessing and reuse of the nuclear materials, the ease of dissolution and purification is an important factor from a waste management point of view. HfN and ZrN appear to be a little harder to dissolve than UN. Thus additions of these nitrides might complicate

the purification and reuse of the spent nuclear fuel. Hard to dissolve materials will generally require more complex processing and more wastes will be generated.

Overall, it is probably an advantage to add ZrN or HfN to the fuel rather than use pure UN. In the near future, there appears to be more support in the U.S. for once through open fuel cycles. In the long-term, as the cost of fuel and waste disposal becomes more expensive, closed cycles will likely become more attractive. In a closed cycle, addition of ZrN or HfN to the fuel may complicate the dissolution and purification process.

Fuel Composition Selection

Based on the criteria of compactness, long-life, proliferation resistance, fuel safety, and waste management some attractive candidates for a modified nitride-based fuel can be selected and evaluated. Overall, TiN does not offer any advantages over ZrN as an inert material so it is not considered further in this first phase of study. Due to current limitations in the LLNL nitride fabrication glove box, additions of ThN and PuN are not considered for the moment. This leaves four parameters: enrichment, UN content, ZrN content, and HfN content.

Table 7 summarizes the four parameters against the five selection criteria. A plus means that the parameter is a slight benefit for that criteria and a minus means that that parameter is a slight detriment to that factor. A zero indicates little or no effect. A double plus indicates a large beneficial effect and a double minus indicates a large detrimental effect.

Table 7. Summary Fuel Selection Criteria

Metric	Enrich.	UN	ZrN	HfN
Compactness	+	0	+	-
Long-Life	++	+	--	+
Prolif. Res.	--	-	+	+
Fuel Safety	0	--	++	++
Waste Man.	0	-	+	+

In summary, the ^{235}U enrichment should be as high as possible with out exceeding 20%. HfN should be added in a suitable amount as a burnable poison, and the balance of the fuel should be ZrN.

Given these criteria, four compositions are suggested for further study in **Table 8**. Case 1 is pure UN with maximum allowable enrichment of ^{235}U. Case 2 is the reference case of UN with 10% enrichment of ^{235}U. Case 3 is an intermediate case with a limited amount of ZrN and HfN added. Ratio of Hf-to-^{235}U is chosen to be 1-to-1. Case 4 is the limiting case where the maximum amount of ZrN is added while limiting the ^{235}U enrichment to 20%. Again the ratio of Hf-to-^{235}U is chosen to be 1-to-1.

Table 8. Selected Compositions for Further Study

	^{235}UN	^{238}UN	ZrN	HfN
Case 1	20	80	0	0
Case 2	10	90	0	0
Case 3	10	70	10	10
Case 4	10	40	40	10

Compositions are given in an atomic or molar basis.

In future studies, additions of ThN and/or PuN may be considered for further study. In terms of compactness and fuel life there could be a significant benefit by replacing ZrN with ^{232}ThN, which has a higher thermal conductivity and breeds during irradiation to ^{233}U. If proliferation concerns in the freshly fabricated fuel can be address by other means, ^{235}U can be replaced by ^{239}Pu in the freshly fabricated fuel.

Conclusion

A study of candidate materials for a modified nitride-based fuel has been completed. The candidate fuels for further study are selected by the potential benefits based on five criteria: compactness, long-life, proliferation resistance, fuel safety, and waste management. The nitrides considered are TiN, ZrN, HfN and ThN with the base nitride fuel being UN or possibly (U,Pu)N.

Overall, there are potentially significant advantages to using modified nitride based fuels. Compositions high in ZrN (or ThN) with a small amount of HfN are recommended for further study.

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7. CONCLUSIONS AND PATHS FORWARD

A manufacturing capability for uranium-based ceramic nuclear fuel was established in LLNL's Fuel Manufacturing Laboratory in B-241. High density oxide fuel including the advanced inert matrix oxide fuel pellets were produced[1] previously with existing equipment. There is a need to upgrade our furnace capability with higher temperature and higher reactant gas fraction in order to produce uranium nitride fuel with the desired stoichiometry, density, and grain structure.

A computational capability to analyze nuclear fuel performance was developed. Industrial-based semi-empirical computer codes (LIFE4Rev1, SIEX3, SPACEPIN, etc.) were acquired and made operational in LLNL computer system. Understanding of the physics models used in these codes should enhance our capability in supporting the multi-scale computational material science development.

Table 1 shows the advanced nuclear fuel development and capability at LLNL.

There were industrial interest and programmatic funding opportunity in our advanced fuel manufacturing capability. Westinghouse and ANL-W (now Idaho National laboratory) were interested in collaborating with us on UN fuel corrosion studies. DOE/NR/KAPL was initiating funding for a SIMFUEL project in LLNL before it was pulled back due to NASA's budget constraint.

Our collaboration with the Nuclear Engineering Department of UC Berkeley on nitride fuel reprocessing and disposal in a geologic repository provided a good opportunity to work with the university faculty and students.

Table 1. Advanced Nuclear Fuel Development and Capability at LLNL

Fuel Type	Applications	Manufacturing Capability	Computational Capability
Mono-uranium Nitride (UN) Fuel	GEN-IV reactor concepts, Space Nuclear Reactor	Making green UN fuel in B-241 Lab. Need to upgrade furnace capability to produce UN fuel with the desired stoichiometry, density, and grain structure	SPACEPIN code can be used to analyze SP-100 irradiated fuel performance data.
Modified Uranium Nitride Fuel	SSTAR, Space Nuclear Reactor	UN fuel with chemical addictives (Zr, Hf, Er, etc)	Need modification of SPACEPIN code for SSTAR
Advanced Oxide Fuel	LWRs, for high burn up	Green pellet made, density >96%TD. Need centerless grinder and new pellet dies to support LWR fuel pellet development	LIFE4Rev1, SIEX3 codes can be used for oxide fuel
Advanced Inert-Matrix (IM) Oxide Fuel	Fast reactors, for non-proliferation applications	Green pellet made with chemical addictives (Zr, Hf), ~94%TD. Need fuel performance data (i.e., irradiation experiment)	Need modification of LIFE4Rev1, SIEX3 for IM oxide fuel

APPENDIX 1. RECORD OF INVENTION – MODIFIED NITRIDE FUEL

IL 11278
Date: October 18, 2004

MODIFIED NITRIDE FUEL FOR COMPACT AND LONG-LIFE REACTORS

The United States Government has rights in this invention pursuant to Contract No. W-7405-ENG-48 between the United States Department of Energy and the University of California for the operation of Lawrence Livermore National Laboratory.

BACKGROUND

Field of Endeavor
The present invention relates to reactors and more particularly to modified nitride fuel for compact and long-life reactors.
State of Technology
United States Patent No. 4,624,828 issued November 25, 1986 to Carl A. Alexander and assigned to Battelle Memorial Institute provides the following state of technology information, "In recent years endeavors have been made to find a nuclear fuel which is compact and produces high temperatures. Such a fuel is of particular value in a nuclear reactor for use in outer space. It is impractical to use metallic uranium for a fuel in such a reactor. This is because of its low melting point and phase changes. Alternative proposals to build stabilized fuels for fast breeder reactors have centered upon the use of uranium dioxide, uranium carbide, and uranium nitride. Also corresponding compounds of thorium, plutonium, or a combination of these elements with uranium fuels have been used. Compatibility is a consideration involved with the selection of any nuclear fuel. The fuel itself must be compatible with the cladding material in which it is contained. The fuel must also be compatible with any materials added to it, such as refractory metals. The addition of a non-compatible element to the fuel may prevent the formation of a satisfactory cermet. For example, carbide nuclear fuels have very limited compatibility with all common materials at elevated temperatures. Another example of incompatibility is present in a composition of uranium mononitride with calcium nitride. The physical properties of this material initially appear to be within the parameters identified for this invention as being required to stabilize a uranium mononitride fuel. However, this material, unlike the nitrides of many transition metals, prevents the formation of a satisfactory cermet with uranium mononitride. Consideration of a material's thermal conductivity compatibility must also be made. Those materials that transfer heat by conduction through electrons have increased thermal conductivity and are preferred over materials that transfer heat primarily by phonon induction. Increased thermal conductivity improves the utility of a nuclear fuel. Uranium dioxide ($UO_\_$) is a very forgiving material. Without problems of significant corrosion to cladding materials or deterioration of cermet formation, it has been shown to be compatible with stainless

steels, refractory metals, and even other ceramics. It is relatively stable and easy to fabricate. It possesses a complex vapor phase and has nearly the poorest thermal conductivity of any potential nuclear fuel. It can be operated for extended periods of time, but only at low temperatures. At high temperatures its operational time is greatly decreased." (Col. 1, lines 11-59, U. S. Patent No. 4,624,828)

SUMMARY

Features and advantages of the present invention will become apparent from the following description. Applicants are providing this description, which includes examples of specific embodiments, to give a broad representation of the invention. Various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this description and by practice of the invention. The scope of the invention is not intended to be limited to the particular forms disclosed and the invention covers all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the claims.

The present invention provides a fuel element for a nuclear reactor. The fuel element comprises a modified nitride uranium or modified nitride plutonium fuel and additives that enhance properties of the modified nitride uranium or modified nitride plutonium fuel. The additives include at least one nitride. In various embodiments nitride additives enhance compactness, long-life, proliferation resistance, fuel safety, and waste management of the fuel element. In various embodiments of the fuel element of the present invention the additives comprise at least one of zirconium nitride, thorium nitride, hafnium nitride, titanium nitride, rare earth nitrides, or other actinide nitrides.

The present invention also provides a method of making a fuel element for a nuclear reactor. The method comprises providing a modified nitride uranium or modified nitride plutonium fuel and adding nitrides to the nuclear fuel to enhance compactness, long-life, proliferation resistance, fuel safety, and waste management properties of the nuclear fuel. In various embodiments of the present invention the step of adding nitrides to the nuclear fuel comprises adding at least one of zirconium nitride, thorium nitride, hafnium nitride, titanium nitride, or rare earth nitrides to the fuel element.

The invention is susceptible to modifications and alternative forms. Specific embodiments are shown by way of example. It is to be understood that the invention is not limited to the particular forms disclosed. The invention covers all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated into and constitute a part of the specification, illustrate specific embodiments of the invention and, together with the general description of the invention given above, and the detailed description of the specific embodiments, serve to explain the principles of the invention.

FIG. 1 shows one embodiment of a fuel rod with UN fuel with additives to enhance fuel properties.

FIG. 2 is a cross section view of the fuel rod shown in figure 1.

DETAILED DESCRIPTION OF THE INVENTION

Referring to the following detailed description, and to incorporated materials, detailed information about the invention is provided including the description of specific embodiments. The detailed description serves to explain the principles of the invention. The invention is susceptible to modifications and alternative forms. The invention is not limited to the particular forms disclosed. The invention covers all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the claims.

Nuclear energy currently supplies twenty percent of the electricity used in the United States and sixteen percent of the electricity used throughout the world. As the global use of nuclear energy grows, so do concerns about the vulnerability of nuclear plants and fuel materials to misuse or attacks by terrorists. A Lawrence Livermore National Laboratory team is part of a Department of Energy (DOE) collaboration that is addressing both the growing need for nuclear energy and the concern over nuclear proliferation by pursuing a concept called Small, Sealed, Transportable, Autonomous Reactor (SSTAR). SSTAR is designed to be a self-contained reactor in a tamper-resistant container. The goal is to provide reliable and cost-effective electricity, heat, and freshwater. The design can also be used to produce hydrogen for use as an alternative fuel for passenger cars.

The SSTAR concept reduces the potential for a terrorist to divert or misuse the nuclear materials and technology. Nuclear fuel will be contained within the sealed, tamper-resistant reactor vessel when it is shipped to its destination, and the spent reactor core will be returned to the supplier for recycling. SSTAR addresses proliferation concerns with other features as well. No refueling is necessary during the reactor's operation, which eliminates access to and long-term storage of nuclear materials on-site. The design also includes detection and signaling systems to identify actions that threaten the security of the reactor. And because of the reactor's small size and its thermal and nuclear characteristics, the design can include a passive method to shut down and cool the reactor in response to hardware or control failures. With fast-moving neutrons, SSTAR could produce the fissile material it needs to fuel continued operation at the same time that it generates energy. Spent fuel in the form of uranium and plutonium would remain in the reactor to generate power for up to 30 years. The spent reactor would then be returned to a secure recycling facility to close the fuel cycle and to minimize the high-level wastes generated by nuclear reactors, thus reducing the space and infrastructure needed for the long-term storage of radioactive wastes. The concept for recycling is to have almost all of the waste burned in the reactor's core.

Materials for the fuel and coolant boundary in the SSTAR concept must be compatible with the coolant. Lead, especially when alloyed with bismuth, tends to corrode the fuel cladding and structural steel. Controlling the oxygen in the coolant will help reduce corrosion. In addition, materials that best withstand the damaging effects of long-term exposure to fast neutrons must be used. Structural damage could include material swelling and ductility loss, both of which may limit the life of the reactor.

The present invention provides UN or (U,Pu)N fuel produced with additives to enhance fuel properties. The enhanced properties include thermal conductivity,

thermodynamic stability, and neutron capture properties. The additives include TiN, ZrN, HfN, ThN, rare earth nitrides, and other actinide nitrides. The enhanced properties lead to potential benefits in the compactness of the reactor design, the life of the reactor, the proliferation resistance both before and after irradiation, the fuel safety, and the waste management of the spent fuel. The enhanced properties are useful for security, such as sealed and long-life fuels, integral instrumentation and control, and specialized detection and signaling systems will be incorporated to minimize the risk of diversion of nuclear materials. The present invention has uses in the SSTAR and other small, compact, and long-life reactors.

Referring to FIG. 1, an embodiment of a fuel rod system incorporating the present invention is illustrated. The system is designated generally by the reference numeral 100. The system 100 includes UN or PuN fuel 102 produced with additives to enhance fuel properties. The system 100 includes a fuel section 104 and a plenum section 106. A cladding 101 encompasses the fuel rod system 100. The fuel rod system 100 includes a liner 103 that provides a chemical barrier. The UN or PuN fuel 102 is in the form of pellets.

Referring to FIG. 1, a cross section view of the fuel rod of FIG. 1 is shown. The fuel rod system 100 includes a liner 103 that provides a chemical barrier. The cladding 101 surrounds the liner 103. The UN or PuN fuel 102 is in the form of pellets. A helium filled gas gap 106 is located between the liner 103 and the fuel pellets 102.

The uranium mono-nitride fuel has favorable properties including its high actinide density and high thermal conductivity. The thermal conductivity of mono-nitride is 10 times higher than that of oxide (23 W/m⁻K for UN vs. 2.3 W/m⁻K for UO_2 at 1000 K) and its melting temperature is much higher than that of metal fuel (2630°C for UN vs. 1132°C for U metal). It also has relatively high actinide density, (13.51 gU/cm^3 in UN vs. 9.66 gU/cm^3 in UO_2) which is essential for a compact core design.

The UN or PuN fuel 102 comprises a modified nitride uranium or modified nitride plutonium fuel and additives that enhance properties of the modified nitride uranium or modified nitride plutonium fuel. The additives include at least one nitride. In various embodiments nitride additives enhance compactness, long-life, proliferation resistance, fuel safety, and waste management of the fuel element. In various embodiments of the fuel element of the present invention the additives comprise at least one of zirconium nitride, thorium nitride, hafnium nitride, titanium nitride, or rare earth nitrides.

Embodiments of the modified nitride-based uranium or plutonium fuel (UN or PuN) fuel 102 has been produced at the Lawrence Livermore National laboratory by carbothermic reduction of oxides in a controlled glovebox environment. The modified nitride-based uranium or plutonium fuel of these embodiments includes additives to enhance five individual properties. The five individual properties are: (1) compactness, (2) long-life, (3) proliferation resistance, (4) fuel safety, and (5) waste management. The uranium or plutonium mono-nitride fuel of these embodiments has uses in the SSTAR and other small, compact, and long-life reactors.

(1) Compactness - The enhanced properties of the uranium or plutonium mono-nitride fuel of these embodiments provide compactness. Higher density of the fissionable isotope (^{235}U) provides a more compact reactor because the critical mass will be smaller.

A smaller core will yield more heat per unit area and higher thermal conductivity of the fuel will be required to get the heat out of the system and maintain an acceptable centerline temperature of the fuel. The composition of the fuel is modified to increase the thermal conductivity without decreasing the density of the ^{235}U in the fuel or affecting the stability of the fuel, a more compact reactor design.

(2) Long-life - Long -life is obtained largely by the reactor design. But fuel composition can also affect the life favorably or unfavorably. The favorable features are:
- High fissile loading (i.e., high ^{235}U enrichment in UN, or high ^{239}Pu content in (U,Pu)N),

- Presence of ^{232}Th or ^{238}U which are converted during irradiation into ^{233}U-rich uranium and ^{239}Pu-rich plutonium, respectively

- Low cladding strain which is dependent upon the fuel centerline temperature and the radiation effects on the fuel and cladding materials

- Presence of burnable neutron poisons in the fuel.

Proliferation concerns limit the ^{235}U enrichment and cladding strain caused by radiation effects. Since the SSTAR is a fast spectrum reactor with a peak neutron energy between 0.2 and 0.3 MeV, the use of burnable poisons will be considerably less effective than in thermal spectrum reactors. The neutron absorption cross sections of various elements at a neutron energy of 0.1 and 0.5 MeV are relatively low, even for many elements that are normally identified as good neutron poisons. Of all these elements, Eu is the best neutron poison in this energy regime, and Hf, Sm, Gd, and Dy are all considerably better than average neutron poisons. The fission cross sections of some of the actinides show that the fission cross section of ^{235}U and ^{239}Pu are roughly the same as Eu and about a factor of four higher than Hf, Sm, Gd, and Dy. Therefore, the rate of neutron capture by one of the burnable poisons will be a little less but still comparable to the rate of fission of the ^{235}U. Even though the neutron absorption cross sections are relatively low in this energy regime, burnable poisons could still lengthen fuel life significantly.

(3) Proliferation Resistance - Proliferation resistance is ensured primarily by the reactor design, but composition of the fuel is also a significant consideration. To ensure that the uranium in the fresh fuel is not attractive for use in nuclear weapons, the ^{235}U enrichment is limited to 20%. The fresh fuel is made even less attractive for diversion by the addition of other inert materials that are not readily separated from UN. Addition of inert materials that are harder than UN to dissolve in aqueous solutions enhances the proliferation resistance. Once the material is dissolved in solution, a PUREX-like purification process will provide good separation of the actinindes from the other inert materials.

Proliferation resistance is a consideration in the spent nuclear fuel, especially if the fuel will be reprocessed. If there is ^{232}Th or ^{238}U in the fresh fuel, the irradiation will lead to ^{233}U-rich or ^{239}Pu-rich weapons useable material in the spent fuel. The attractiveness of the Pu is reduced, but not eliminated, by the presence of higher enrichments of ^{235}U in the fresh fuel. Under irradiation, ^{237}Np and to a lesser extent ^{235}U are eventually converted into to ^{238}Pu. The attractiveness of the plutonium in the irradiated fuel is also reduced, but not eliminated, by longer irradiation times, e.g. higher

burn-ups. The long irradiation cycle (as supported by the long life of the reactor fuel) will render the spent fuel with a higher percentage of ^{240}Pu and ^{242}Pu.

Overall, the attractiveness of the fresh fuel is reduced very little by additions of other nitrides to the UN fuel, and the attractiveness of the spent fuel is reduced some by minimizing the ^{238}U content relative to the ^{235}U content as long as the ^{235}U enrichment is kept below 20%.

(4) Fuel Safety - For nitride fuel and cladding, the relevant criteria for fuel safety are
- Fission gas release and retention
- Fuel pellet cladding interaction
- Radiation swelling effects
- Fuel centerline temperature

In general, the attainable burn-up and thus operating life of nuclear fuels are limited by materials performance issues, which result from changes in the thermal and mechanical properties and dimensional stability of the fuel pellets, cladding and structural materials during neutron irradiation. The development of modified nitride fuel provides improved materials and design approaches in order to reach higher burn-ups.

The effects of fission gas build-up can be mitigated by the fuel pin design. If the density of the fuel is low enough that the porosity is open, usually around 95% of theoretical or less, the fission gases will be able to diffuse out of the fuel and collect in the gaps at the ends of the fuel pins. Modification of the fuel composition is not a benefit or detriment in this respect. The stability of the fuel with the cladding is dependent upon the thermodynamic stability, compatibility of the materials, the fuel temperature, and radiation induced swelling effects.

The temperatures where oxidation of the nitride powder begins and the temperature at which the powder ignites is important. For bulk solids, these temperatures will of coarse be much higher. Data shows that additions of any of the nitrides except PuN will benefit the oxidation resistance and possibly simplify considerably the handling of the material. The best nitrides to add to the fuel matrix are clearly ZrN and HfN.

In regards to interaction with the cladding some thermodynamic calculations can be performed to see if the nitrides are stable with respect to the cladding materials, which are taken to be a zirconium-rich alloy (normally for heavy and light water reactors) , a niobium-rich alloy (normally for space reactors), or a iron-based alloy (normally for liquid metal reactors). These calculations show that these additives significantly increase the stability of the modified nitride fuel with respect to the fuel element cladding.

(5) Waste Management - Waste management is a complicated issue with spent nuclear fuel. If the fuel is to be used in a once through cycle and disposed of directly, it will be important that the fuel is stable for thousands of years in an underground repository. If the fuel is to be used in a close cycle, it will be important that the fuel can be easily purified and reused.

For an open once through fuel cycle, the spent fuel will eventually need to be disposed of in an underground repository. Since the components in the fuel will not be reused, it is best from a proliferation point of view to dispose of the fuel directly and not separate the fission products from the actinides thus making them attractive for theft or diversion. Nitrides are more reactive than oxides so the case for direct disposal may be

more difficult. Addition of nitrides except PuN to the UN fuel will significantly stabilize the fuel making it more stable with respect to water and more resistant to oxidation. Thus, it is a significant advantage from the waste management point of view for a direct disposal option to add TiN, ZrN, HfN, or ThN to the UN fuel.

For a closed fuel cycle involving reprocessing and reuse of the nuclear materials, the ease of dissolution and purification is an important factor from a waste management point of view. HfN and ZrN appear to be a little harder to dissolve than UN. Thus additions of these nitrides might complicate the purification and reuse of the spent nuclear fuel. Hard to dissolve materials will generally require more complex processing and more wastes will be generated.

Overall, it is an advantage to add ZrN or HfN to the fuel rather than use pure UN. There appears to be more support in the U.S. for once through open fuel cycles. In the long-term, as the cost of fuel and waste disposal becomes more expensive, closed cycles will likely become more attractive. In a closed cycle, addition of ZrN or HfN to the fuel may complicate the dissolution and purification process.

In a closed cycle, long lived actinide wastes (namely NpN and AmN) can be dispositioned in the fuel. In the case of ^{237}Np, it is converted to ^{238}Pu during irradiation, thus making the overall Pu isotopic composition of the fuel less desirable for weapons use.

In various embodiments of the present invention nitride additives enhance compactness, long-life, proliferation resistance, fuel safety, and waste management of the fuel element. Examples of the various embodiments of the fuel element of the present invention will now be described. In the various examples the additives comprise at least one of zirconium nitride, thorium nitride, hafnium nitride, titanium nitride, rare earth nitrides, or other actinide nitrides.

Example 1

A modified nitride-based uranium fuel has been produced at the Lawrence Livermore National laboratory by carbothermic reduction of oxides in a controlled glovebox environment. The modified nitride-based uranium fuel of Example 1 comprises ten percent uranium-235 (10% UN), forty percent zirconium nitride (40% ZrN), ten percent hafnium nitride (10% HfN), and forty percent uranium-238 (40% UN). The modified nitride-based uranium fuel of Example 1 or variants of Example 1 can be used by fuel fabricators that are not authorized to handle ^{233}U or Pu (i.e. most companies) and who wish to make a nitride fuel that is suitable for use in heavy or light water reactors (i.e. resistant to reaction with water).

The enhanced properties of the modified uranium mono-nitride fuel in Example 1 lead to potential benefits in the compactness of the reactor design, the life of the reactor, the proliferation resistance both before and after irradiation, the fuel safety, and the waste management of the spent fuel. The enhanced properties are useful for security, such as sealed and long-life fuels, integral instrumentation and control, and specialized detection and signaling systems will be incorporated to minimize the risk of diversion of nuclear materials. The modified uranium mono-nitride fuel in Example 1 has uses in the SSTAR and other small, compact, and long-life reactors.

The enhanced properties of the modified uranium mono-nitride fuel of Example 1 provide compactness. Higher density of the fissionable isotope (^{235}U) provides a more compact reactor because the critical mass will be smaller. A smaller core will yield more heat per unit area and higher thermal conductivity of the fuel will be required to get the heat out of the system and maintain an acceptable centerline temperature of the fuel. The composition of the fuel is modified to increase the thermal conductivity without decreasing the density of the ^{235}U in the fuel or affecting the stability of the fuel, a more compact reactor design.

Example 2

Another example of a modified nitride-based fuel for a nuclear reactor has been produced at the Lawrence Livermore National laboratory by carbothermic reduction of oxides in a controlled glovebox environment. The modified nitride-based fuel of Example 2 comprises ten percent plutonium (10% Pu), ten percent zirconium nitride (10% ZrN), ten percent hafnium nitride (10% NpN), and seventy percent uranium-238 (70% UN). The enhanced properties of the mono-nitride fuel of Example 2 or variants of the mono-nitride fuel of Example 2 can be used by countries that are interested in reprocessing the spent fuel and recovering and using the Pu.

Example 3

Another example of a modified nitride-based fuel for a nuclear reactor has been produced at the Lawrence Livermore National laboratory by carbothermic reduction of oxides in a controlled glovebox environment. The modified nitride-based fuel of Example 3 comprises a mixture of ten percent of uranium-233/ uranium-235, seventy percent thorium nitride (70% ThN), ten percent zirconium nitride (10% ZrN), ten percent hafnium nitride (10% HfN). The enhanced properties of the mono-nitride fuel of Example 3 or variants of the mono-nitride fuel of Example 3 can be used be used by countries with abundant Th resources and are interested in reprocessing the spent fuel and recovering and using the ^{233}U.

Example 4

Another example of a modified nitride-based fuel for a nuclear reactor has been produced at the Lawrence Livermore National laboratory by carbothermic reduction of oxides in a controlled glovebox environment. The modified nitride-based fuel of Example 4 comprises ten percent plutonium (10% Pu), seventy percent zirconium nitride (70% ZrN), ten percent hafnium nitride (10% NpN), and ten percent neptunium nitride (10% NpN) or ten percent americium nitride (10% AmN). The enhanced properties of the mono-nitride fuel of Example 4 or variants of the mono-nitride fuel of Example 4 can be used to disposition plutonium. The resulting fuel would be high in ^{238}Pu, ^{241}Pu, and ^{242}Pu. The Np and Am would also be consumed.

The invention is susceptible to various modifications and alternative forms. Specific embodiments have been shown by way of example in detail herein. It is to be understood that the invention is not intended to be limited to the particular forms disclosed. Rather, the invention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the following appended claims.

THE INVENTION CLAIMED IS

Claim 1. A fuel element for a nuclear reactor, comprising:

a modified nitride uranium or modified nitride plutonium fuel; and

additives that enhance properties of said modified nitride uranium or modified nitride plutonium fuel, said additives comprising at least one nitride.

Claim 2. The fuel element of claim 1 wherein said additives comprise at least one of zirconium nitride, thorium nitride, hafnium nitride, titanium nitride, rare earth nitrides, or other actinide nitrides.

Claim 3. The fuel element of claim 1 wherein said additives include zirconium nitride.

Claim 4. The fuel element of claim 1 wherein said additives include hafnium nitride.

Claim 5. The fuel element of claim 1 wherein said nuclear fuel comprises ten percent uranium-235 and said additives comprise forty percent zirconium nitride and ten percent hafnium nitride, and including forty percent uranium-238.

Claim 6. The fuel element of claim 1 wherein said nuclear fuel comprises ten percent plutonium and said additives comprise ten percent zirconium nitride and ten percent hafnium nitride, and including seventy percent uranium-238.

Claim 7. The fuel element of claim 1 wherein said nuclear fuel comprises ten percent of a mixture of uranium-233 and uranium-235 and said additives comprise seventy percent thorium nitride, ten percent zirconium nitride, and ten percent hafnium nitride.

Claim 8. The fuel element of claim 1 wherein said nuclear fuel comprises ten percent plutonium and said additives comprise seventy percent zirconium nitride, ten percent hafnium nitride, and ten percent neptunium nitride or ten percent americium nitride.

Claim 9. A fuel rod for a nuclear reactor, comprising:

a fuel rod liner,

a nuclear fuel positioned in said fuel rod liner, said nuclear fuel comprising modified nitride uranium or modified nitride plutonium fuel; and

nitrides additives to enhance properties of said nuclear fuel, said properties comprising compactness, long-life, proliferation resistance, fuel safety, and waste management.

Claim 10. A fuel element for a nuclear reactor, comprising:

nuclear fuel, said nuclear fuel comprising modified nitride uranium or modified nitride plutonium fuel; and

additive means for enhancing compactness, long-life, proliferation resistance, fuel safety, and waste management properties of said nuclear fuel.

Claim 11. The fuel element of claim 10 wherein said additive means comprises at least one of zirconium nitride, thorium nitride, hafnium nitride, titanium nitride, rare earth nitrides, or other actinide nitrides.

Claim 13. The fuel element of claim 10 wherein said additive means include zirconium nitride.

Claim 14. The fuel element of claim 10 wherein said additive means include hafnium nitride.

Claim 15. The fuel element of claim 10 wherein said nuclear fuel comprises ten percent uranium-235 and said additive means comprise forty percent zirconium nitride and ten percent hafnium nitride, and including forty percent uranium-238.

Claim 16. The fuel element of claim 10 wherein said nuclear fuel comprises ten percent plutonium and said additive means comprise ten percent zirconium nitride and ten percent hafnium nitride, and including seventy percent uranium-238.

Claim 17. The fuel element of claim 10 wherein said nuclear fuel comprises ten percent of a mixture of uranium-233 and uranium-235 and said additive means comprise seventy percent thorium nitride, ten percent zirconium nitride, and ten percent hafnium nitride.

Claim 18. The fuel element of claim 10 wherein said nuclear fuel comprises ten percent plutonium and said additive means comprise seventy percent zirconium nitride, ten percent hafnium nitride, and ten percent neptunium nitride or ten percent americium nitride.

Claim 19. A method of making a fuel element for a nuclear reactor, comprising:
providing a nuclear fuel comprising modified nitride uranium or modified nitride plutonium fuel; and
adding nitrides to said nuclear fuel to enhance compactness, long-life, proliferation resistance, fuel safety, and waste management properties of said nuclear fuel.

Claim 20. The method of making a fuel element of claim 19 wherein said step of adding nitrides to said nuclear fuel comprises adding at least one of zirconium nitride, thorium nitride, hafnium nitride, titanium nitride, or rare earth or actinide nitrides to said fuel element.

Claim 21. The method of making a fuel element of claim 19 wherein said step of adding nitrides to said nuclear fuel comprises adding zirconium nitride to said fuel element.

Claim 22. The method of making a fuel element of claim 19 wherein said step of adding nitrides to said nuclear fuel comprises adding hafnium nitride to said fuel element.

Claim 23. The method of making a fuel element of claim 19 wherein said nuclear fuel comprises ten percent uranium-235 and including forty percent uranium-238, and said step of adding nitrides to said nuclear fuel comprises adding forty percent zirconium nitride and ten percent hafnium nitride to said fuel element.

Claim 24. The method of making a fuel element of claim 19 wherein said nuclear fuel comprises ten percent plutonium and including seventy percent uranium-238, and said step of

adding nitrides to said nuclear fuel comprises adding ten percent zirconium nitride and ten percent hafnium nitride to said fuel element.

Claim 25. The method of making a fuel element of claim 19 wherein said nuclear fuel comprises ten percent of a mixture of uranium-233 and uranium-235 and said step of adding nitrides to said nuclear fuel comprises adding seventy percent thorium nitride, ten percent zirconium nitride, and ten percent hafnium nitride to said fuel element.

Claim 26. The method of making a fuel element of claim 19 wherein said nuclear fuel comprises ten percent plutonium and said step of adding nitrides to said nuclear fuel comprises adding seventy percent zirconium nitride, ten percent hafnium nitride, and ten percent neptunium nitride or ten percent americium nitride said fuel element.

ABSTRACT OF THE DISCLOSURE

A fuel element for a nuclear reactor comprises a modified nitride uranium or modified nitride plutonium fuel and additives that enhance properties of the modified nitride uranium or modified nitride plutonium fuel. In various embodiments nitride additives enhance compactness, long-life, proliferation resistance, fuel safety, and waste management of the fuel element. In various embodiments the additives comprise at least one of zirconium nitride, thorium nitride, hafnium nitride, titanium nitride, or rare earth nitrides.

MODIFIED NITRIDE FUEL FOR COMPACT AND LONG-LIFE REACTORS

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APPENDIX 2.   NR/KAPL UO$_2$ SIMFUEL PROJECT

STATEMENT OF WORK:

To support Knolls Atomic Power Laboratory (KAPL)'s Space Reactor Fuel and Material Research Program for DOE Naval Reactor Operation (NRO), by manufacturing simulated UO$_2$ fuel (SIMFUEL) with inclusion of constituent powders and additional chemical additives. The weight % of the fission-product element-inclusions will be calculated by ORIGEN2 for 2 burn-up formulas (2 and 4 atomic %).

Specifications for the UO$_2$ SIMFUEL are listed below:

Burn-up Formulas: 2 and 4 Atomic %

Amount: 2.5 kilograms total, 1.25 kilograms for each formula

Constituent Powders: at least 2 to 3 nines purity, -325 mesh/-44 micron particle size
                    UO$_2$, BaCO$_3$, CeO$_2$, La$_2$O$_3$, MoO$_3$, SrO, Y$_2$O$_3$, ZrO$_2$, Rh$_2$O$_3$, PdO, RuO$_2$, Nd$_2$O$_3$

Additional Chemical Additives: Xe, Cs (specific methods attached)

Pressed Pellet Dimensions: Approximately _" diameter, approximately _" height, 3 to 5 weight per pellet – there is flexibility in these specs, depending on the size and die sets at LLNL

Fabrication Method: Based on the technique demonstrated in LLNL's UO$_2$ and inert matrix fuel pellet fabrication[1], and methods used by others[2,3]. Deviations from these methods are expected due to present furnace limitations and die set size for pellet pressing

Material Analysis, Post-Sintering: Analytical examination of the sintered pellets, including chemical, density and material characterization analysis will be performed for both formulas

Procurement: LLNL will consider at the beginning of the project the purchase of the Red Devil Vacuum Furnace from the R. D. Webb Company. The new furnace will have a higher temperature capability. LLNL will also consider the purchase of a hot press during the course of the project for Cs incorporation

Project Duration: Starting from August 2005 (FY'05), the completion of the project is anticipated in FY'07. LLNL will first run test batch (50 to 100g) of the 2 and 4 at% formulas and perform characterization analysis of the pellets. Upon the acceptability of the product of these test runs, LLNL will proceed with production runs on the balance of 1.25 kg for each formula

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Cesium Inclusion

In the plutonium immobilization program that was conducted during the late 1990's, LLNL made a number of cold press and sintered ceramic SYNROC samples with cesium. Because of its volatility much, but not all of the cesium, was lost during the sintering process. From this experience we conclude that UO_2 SIMFUEL with cesium can be prepared by over doping the fuel with cesium before sintering.

During sintering, it is expected that a fraction of the cesium will be lost. The approach we take is to estimate the amount of over-doping cesium needed to produce the approximately right amount of cesium in the final products of 2 and 4 atom% burn-up. The installation of a new vacuum furnace where the partial pressure of argon could be maintained could help in minimizing the cesium loss during sintering. This approach has several potential problems. The density of the product may be reduced due to the cesium volatility.! It will also be difficult to reach the exact target cesium concentration.

Ion Beam Laboratory, Lawrence Livermore National Laboratory (LLNL)

Ion beam capabilities available in LLNL's Materials Science and Technology Division include a 4MV Pellatron Van de Graaf accelerator and a 200 kV implanter.   These machines provide isotopically pure beams of ions from 1 amu (protons) to 131 amu (xenon) at high current. Helium ions, for example, can be accelerated to energies as high as 8 MeV with our equipment. In the parlance of nuclear physics such ions are known also as alpha particles and they are commonly created by radioactive sources and in nuclear reactors. Having the ability to subject materials to alpha irradiation without making the samples radioactive has been used to eliminate difficult ES&H issues that hinder studies of radiation damage and aging of radioactive materials. Our experiments are non hazardous since radioactive materials are not required or generated. Also, we have accurate dosimetry and energy control. We will provide currents as high as 10 microamps (6.25×10^{13} alpha particles per second) into a foot print as small as 0.4 cm^2. The samples can be cooled if necessary.

In general, the energy and mass of the ions is set to provide the desired energy loss per unit length, the ratio of nuclear stopping to electronic stopping, and whether the ion passes through the object or comes to rest inside. The dose can be accurately controlled over 1 x 10^6 ions/cm^2 to 1 x 10^{18} ions/cm^2 and the dose rate from 1 x 10^9 ions/sec to 1 x 10^{16} ions/sec, respectively. In the case Xe, which we can accelerate to 20 MeV, speed, the energy deposition, and mass of the of the ion mimics quite accurately fission fragments, which are the most damaging of the species found in nuclear technologies. Uranium recoil ions are far less damaging than fission products, but also prevalent in technological applications. Our equipment easily produces the parameters that accurately mimic these species.

REFERENCES:

1.   T. Meier, S. Fossett, B. Ebbinghaus, J. Choi, „C&MS Science and Technology Project: Demonstration of UO_2 and Inert Matrix Fuel Pellet Fabrication," LLNL, 30 September 2002.
2.   A. K. Sengupta, et.al., "Some important properties of simulated UO_2 fuel," BARC/1999/E/008, Bhabha Atomic Reserch Centre, Mumbai, India, 1999.
3.   P. G. Lucuta, et. Al., "Microstructural features of SIMFUEL – simulated high-burnup UO_2-based nuclear fuel," Journal of Nucl. Matl. 178, 48-60, 1991.

APPENDIX 2.   REPROCESSABILITY AND PERFORMANCE IN GEOLOGIC REPOSITORY OF MONO-NITRIDE FUEL

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September 2005

<u>Scope of Work</u>

Objective:

This LDRD project is aimed at establishing fundamental bases for manufacturing and modeling capabilities for mono-nitride fuel. In the modeling capability area, the team at UCB will be in charge of analyzing (1) reprocessing processes for nitride fuels and (2) performance and safety of nitride fuel if it is disposed of in a geologic repository, such as Yucca Mountain repository.

Background:

The three-year LDRD is being carried out at Lawrence Livermore National Laboratory, to initiate advanced fuel development effort at LLNL and enhance its capability in material sciences research and manufacturing for mono-nitride fuel for the use in compact long-life reactors such as a liquid-metal cooled small reactor (SSTAR) and a light liquid-cooled reactor designed for space applications.

In the first and second years, various computer codes were acquired and modified for fuel performance and burn-up of nitride fuel. A lab-scale uranium-based nitride fuel manufacturing system was installed at LLNL. A flow sheet for nitride fuel fabrication was developed. With the system, a few sintered pellets of UN were made. UN and UN+ZrN+HfN were compared from various viewpoints including compactness, proliferation resistance, and fuel safety.

The tasks to be performed by the team at UCB will add important viewpoints for comparison, i.e., reprocessability and repository performance.

Scope of Work:

The following areas of work are to be addressed by the UCB team:

Task 1: Preliminary literature survey for (1) reprocessing of irradiated mono-nitride fuel and for (2) geochemical reactions of nitride fuel with groundwater

Task 2: Analyses on reprocessing process for mono-nitride fuel

Task 3: Analyses on dissolution mechanisms of nitride fuel in geologic environment to evaluate performance in a geologic repository.

Task 4: Prepare input for the LDRD final report. The UCB study report will be combined with the reports on other activities in the project.

Executive Summary

To investigate reprocessability and performance in a geologic repository for mono-nitride fuel, mathematical models have been developed.

For reprocessability, a pyrochemical process method is considered because evolution and recycle of N-15 gas can be handled. A simplified model reprocessing scheme has been analyzed for the separation of uranium mono-nitride fuel from cerium mono-nitride with a multi-stage extraction system. The distribution coefficient obtained from an optimized single-stage extraction system has been utilized as input data for a multi-stage extraction system. With 10 stages, the overall purity of the recovered uranium was 98.9% in the multi-stage extraction system with a net uranium recovery of 79%.

For repository performance, the dissolution rate for UN would be much lower than that for U metal but higher than that of uranium silicide. The reported high dissolution rates of UN in water at ~ 92°C indicate that UN is not stable in the hot aqueous environment. The numerical evaluation, based on the assumption that the dissolution rate of UN spent fuel is 10 times greater than those for UO$_2$ and borosilicate glass, indicates that the dissolution of UN spent fuel would complete within the time duration comparable to the half-life of Pu-239.

Thus, while UN may be a good fuel for a reactor that uses a non-aqueous coolant and is operated with a reprocessing option, spent UN fuel will be poor waste form for permanent disposal in a geologic repository because of its reactivity in an aqueous environment.

<u>Reprocessability Analysis</u>

Introduction

Uranium mononitride is being considered as a potential nuclear fuel for encapsulated nuclear heat sources, transmutation of toxic long-lived actinides, and space satellite missions. Numerous reactor performance studies have been performed with UN and it has been determined that the fuel has several desirable properties, which triggered an increased interest in the fuel.

Uranium mononitride is oxidized by heated water vapor, generating ammonia[1]:

$2UN + 4H_2O \rightarrow 2UO_2 + 2 NH_3 + H_2$

Thus, with an appropriate pre-treatment, UN spent fuel can be reprocessed by conventional PUREX process. However, mainly because of a potential problem of evolution and recycle of nitrogen-15 gas[2], pyrochemical processes have been considered suitable, and studied actively for this type of fuel.

The present work will focus on a pyrochemical processing method. The system is shown in Figure III.1**.**

Single-Stage Molten-Salt/Liquid Metal Extraction System.

Figure III.2 **below shows a schematic of a single-stage molten-salt/liquid metal extraction system. In the diagram, it is assumed that initially no uranium or cerium are present in the molten-salt phase. Additionally, bismuth and potassium are non-interacting spectator metals in the system. Initially the liquid metal phase containing the lithium reductant is contacted with the molten-salt phase. After a four-hour equilibrium, the phases are cooled and separated. The reductant is molten lithium; the actinides act as the corresponding oxidants. The following equations describe the interactions in the system:**

UCl_3 (salt) + 3Li (metal) ∩ U (metal) + 3LiCl (salt) K_U = 1.12 x 1012   [1]

$CeCl_3$ (salt) + 3Li (metal) ∩ Ce (metal) + 3LiCl (salt) K_{Ce} = 5.75 x 108   [2]

Notice that the equilibrium constant for the uranium reduction is several orders of magnitude higher than the corresponding cerium reduction. This leads us to conclude that for any system, more uranium will always be recovered than cerium except in the limiting case that the mass of UCl_3 is infinitesimal relative the cerium chloride. Note also that given the high equilibrium constants, it is also possible for $CeCl_3$ to *reduce* UCl_3:

UCl_3 (salt) + Ce (metal) ∩ $CeCl_3$ (salt) + U (metal) K_U' = 1.95 x 10^3 [3]

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[1] Bridger et al., Oxidation and hydrolysis of uranium and plutonium nitrides, *Reactivity in Solids, Proceedings of an International Symposium,* Wiley-Interscience, New York, NY, 389-400, 1969.

[2] T. Mukaiyama, OMEGA Program in Japan and ADS Development at JAERI, *Proc. 3rd Int. Conf. Accelerator Driven Transmutation Technologies and Applications,* Prague , 7 - 11 June 1999, Czech Republic.

Chlorination of U,CeN

$2MN + 6Pt \rightarrow 2MPt_3 + N_2$
$2MPt_3 (Cd) + 3CdCl_2(LiCl\text{-}KCl) \rightarrow$
$\qquad 2MCl_3 (LiCl\text{-}KCl) + 6Pt (Cd)$
(or other method, e.g., anodic dissolution)

Reductive Extraction

-Typically a molten-salt system with
  KCl-LiCl eutectic with liquid cadmium
-removes noble metal FP's (i.e.
  transition metals) that are extracted
  into Cd phase

Salt Waste Treatment

-Recover Li for recycling
-Recover Cl_2 for recycling

Molten-Salt/Liquid Metal (Bi,Li) Extraction

-Initially Ln(III)'s and Ac(III)'s are in LiCl-
  KCl eutectic
-Can effectively separate Ac(III) from Ln(III)

Figure III.1: A pyrochemical treatment of uranium mononitride[3].

The magnitude of equilibrium constant for equation [3] implies that the extent of reduction of uranium due to cerium metal is essentially negligible. Thus, in this work, the reduction due to cerium will be neglected.

Several Mass Balance Equations must be introduced so that distribution coefficients for each reacting component of the system can be calculated. Figure III.3 is a collection of all the mass balance equations considered for the calculations. Here μ_j^0 refers to the initial mass of the jth species in the salt phase (e.g., Ce, U) and m_j^0 refers to the jth species in the metal phase initially. Non-superscripted values correspond to the *equilibrium* mass of the species. The values used for this work are shown below in Table III.1.

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[3] Kinoshita, et. al. *J. Nuc. Sci. Tech.*, **36**, 2, 189-197.
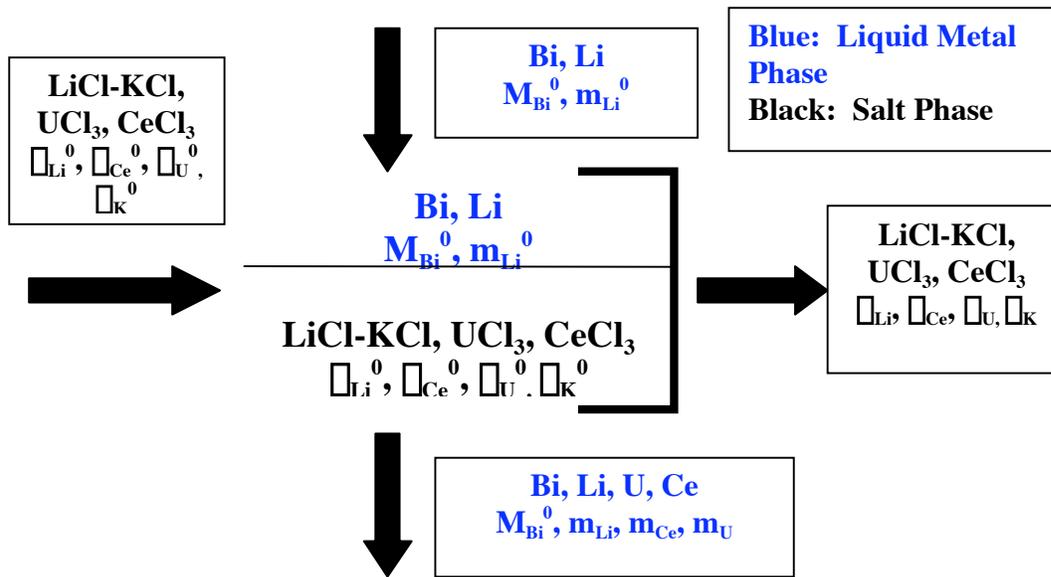
Figure III.2: Simple Molten-Salt/Liquid Metal Extraction System. Here Li is the reductant and the actinide chloride is the oxidant.

$\mu_{TOT} = \mu_{Li} + \mu_K^0 + \mu_U + \mu_{Ce}$ Salt Phase Mass Balance
$m_{TOT} = m_{Bi}^0 + m_{Li} + m_U + m_{Ce}$ Liquid Metal Phase Mass Balance
$\mu_U^0 = \mu_U + m_u$ Total Uranium Balance
$\mu_{Ce}^0 = \mu_{Ce} + m_{Ce}$ Total Cerium Balance
$\mu_{Li}^0 + m_{Li}^0 = \mu_{Li,i} + m_{Li}$ Total Lithium Balance
$m_{Li,i}^0 - m_{Li,i} = 3m_{Ce,i} + 3m_U$ An "Electron Balance"

Figure III.3: Mass Balance Equations Utilized for Optimization of the Single-Stage Extraction System.

Table III.1: **Initial Input conditions for the single stage extraction system.**

1) Parameter	1) Value
2) μ_K^0	2) 0.65 mol
3) μ_{Li}^0	3) 0.95 mol
4) μ_U^0	4) 2.5×10^{-4} mol
5) μ_{Ce}^0	5) 2.5×10^{-3} mol
6) M_{Bi}^0	6) 0.25 mol
7) m_{Li}^0	7) 0.00123 mol
8) K_U	8) 1.12×10^{12}
9) K_{Ce}	9) 5.75×10^8

$$10)R \qquad 10)0.150$$
$$11)q_{Ce} = q_U \qquad 11)3$$

Results

Figure III.4 **shows the extracted uranium as a function of initial lithium loading. As expected, increasing the initial lithium loading increases the amount of extracted uranium increases. With this fact in mind, it would seem that higher quantities of lithium are required to extract the most uranium. However, although the preference of lithium to reduce UCl_3 is greater than that of $CeCl_3$, $CeCl_3$ is also reduced in some quantity. As**
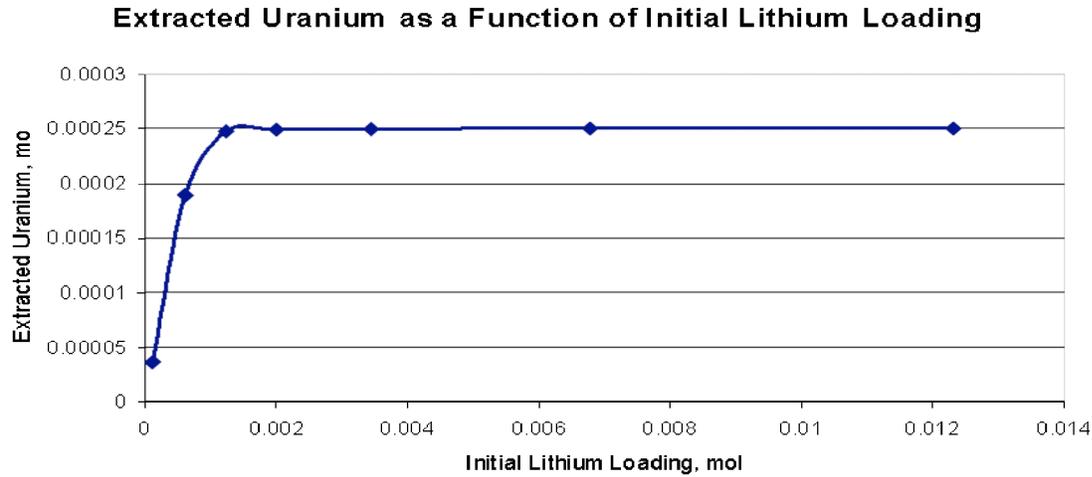
Figure III.4: Extracted Uranium as a Function of Initial Lithium loading.
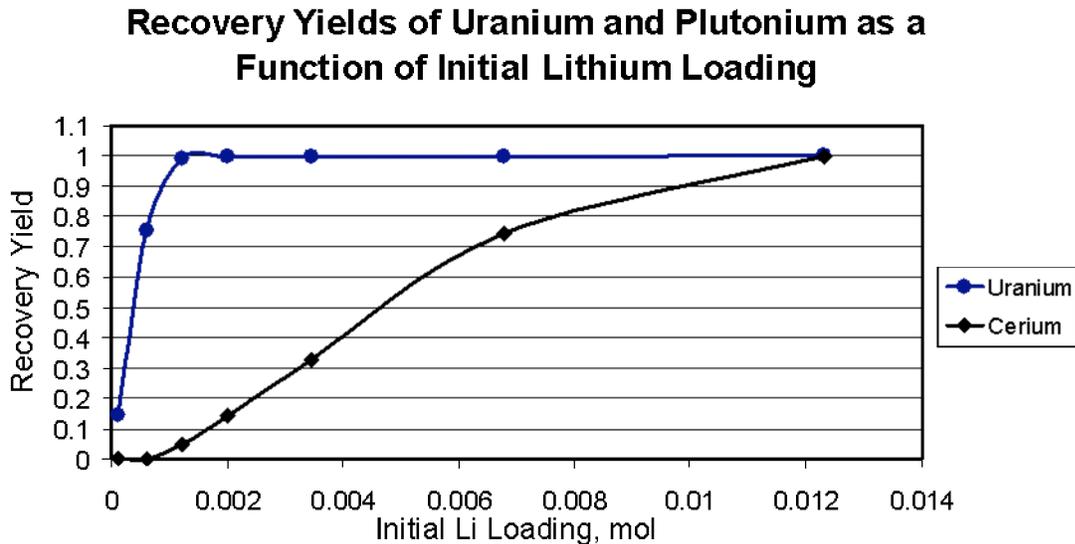
Figure III.5: Recovery Yields of Uranium and Plutonium as a Function of Initial Li loading.

Table III.1 showed, in this system there is more CeCl3 than UCl3 by an order of magnitude. Thus, although more uranium is recovered, there is similarly more cerium recovered. Figure III.5 illustrates this.

Finally, the recovery yield of the uranium tended to decrease with increasing purity. This is depicted in Figure III.6 below. Because the purity of an extracted metal is typically a more important concern than recovery yield, the system values were optimized at a low initial lithium loading (0.000123 mol). To increase the overall yield of uranium with a similar purity, a multi-stage extraction system was developed. It was hoped that several extractions with small recovery yields would give an overall higher recovery yield after n stages than a single-stage extraction system.
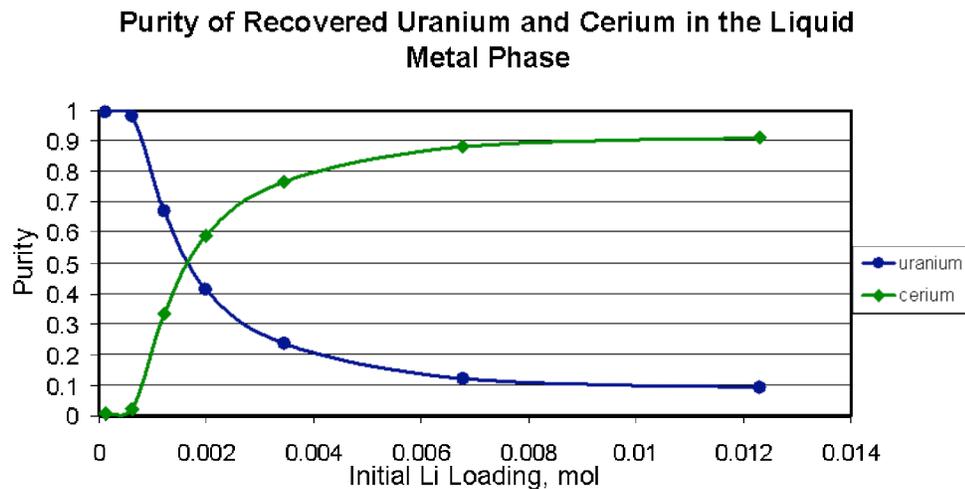
Figure III.6: Purity of U and Ce as a Function of Initial Lithium Loading

Multi-Stage Extraction System

Figure III.7 **below shows a typical extraction system used for this work.**

In this system, a liquid metal phase is contacted with a salt phase. After an equilibrium time, the two phases are decreased and the liquid metal phase collected. The process is repeated whereby the liquid phase is removed and replaced with a fresh quantity of liquid metal. Computationally, the only difference in this system from the single-stage extraction is that the equilibrium concentration for the first stage is equivalent to the initial input value for the next stage. The mass balance equations are the same as those listed in Figure II.2 **above.**

The distribution coefficient that corresponded to the highest purity and lowest recovery yield was utilized to maintain the purity of the recovered uranium in each step. Using this value, it could be determined the initial lithium loading mass m_{Li}^0 at each stage.

Figure III.8 **shows the cumulative recovery yield and purity calculated in this work. Although the purity slightly decreased at each step, there was a cumulative purity of 98.9%. More work must be done to determine why the purity decreased at each step.**

In theory, one can determine the number of stages required to extract all of the uranium from the liquid phase by extrapolating the cumulative recovery yield to 1. The cumulative uranium

purity at that stage would give an idea of the overall purity of the uranium at nearly 100% separation.

Also, if both curves are extrapolated to the point where they cross, one can determine the number of stages that optimizes both the yield and the purity (both near 100%).

As a proof of concept measurement the values were obtained for a ten-stage system since most literature quotes five to ten stages. After 10 stages, the cumulative purity was determined to by 98.9%; the cumulative yield was only 79%.
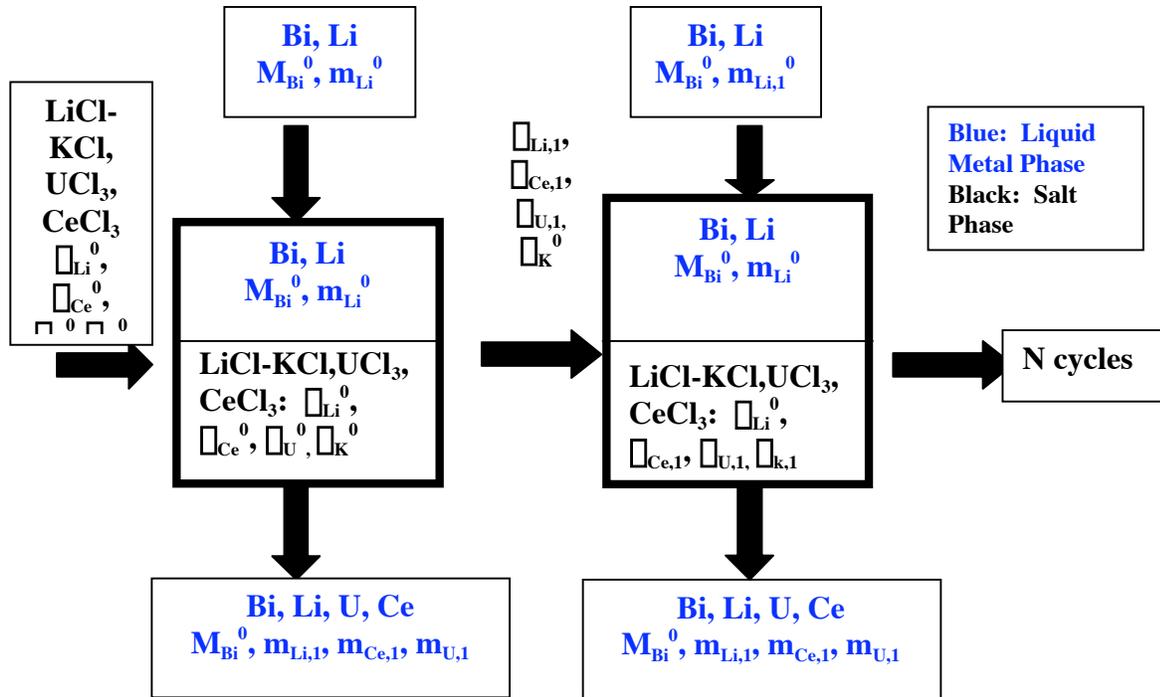
Figure III.7: Multi-Stage Extraction System.

Figure III.8: Cumulative Purity and Recovery Yield as a function of stage number. Note the steady increase in recovery but slight decrease in purity.

Summary

In general, the net recovery yield of uranium from the multi-stage extraction was higher after 10 stages than in the simple single-stage extraction step. However, the net purity of the uranium extracted seemed to decrease slightly after each extraction, leading to a net purity of 98.9% as opposed to 99.4% extraction in the single-stage extraction system. This fact appears to be a result of one of two things. First, the constant lithium distribution coefficient may be invalid in that it slightly overestimates the amount of lithium loading needed for each step. This overestimate causes more cerium to be extracted as well. At each step there needs to be a new iteration to find the lithium distribution coefficient with an initial mass loading guess.

The value of r, 0.150, was assumed to be constant. This is perhaps a poor approximation because after each extraction, the liquid metal phase is removed and replaced by fresh Bi-Li alloy. Also, if the amounts of bismuth and potassium are supposedly constant, it would be necessary to recalculate r because the mass ratios are no longer constant. Because such an assumption was made for this project, the value "r" would need to be recalculated for each stage. Otherwise, the total amount of mass in each phase may be made to be constant by varying the initial potassium and bismuth masses but that would change the composition of each phase. For an accurate model of the system, such changes have to be taken into account. Either of the abovementioned situations may explain the slight decrease in purity values.

In the future, this system may be compared to a "counter-current" multi-stage extraction system. The major difference between this system and the multi-stage extraction system proposed in this work is that instead of removing each liquid metal phase after equilibration, it is shuffled into a second stage with a counter-flowing salt phase that contacts the liquid metal phase and is equilibrated. It is expected that this system will generate higher recoveries and purities over fewer stage numbers because in each stage of the extraction, the liquid metal stage is in contact with fresh salt phase. The net effect is that the purity and recovery yield of the uranium in the metal phase increases steadily because the liquid metal phase is essentially "scrubbed" by the salt phase.

Repository Performance Analysis

Introduction

To consider repository performance for high-level waste (HLW), the principal importance is the rate of dissolution of matrix material by reacting with groundwater in repository environment. The rate of dissolution into groundwater is determined by various factors, such as in-package chemistry and temperature, which are determined by drift tunnel layout in the repository, hydro-geological conditions in the host rock, chemical compositions of groundwater, and materials contained in the waste package.

The matrix material is either fuel material itself in case spent fuel is directly disposed of, or solidification material after reprocessing such as borosilicate glass. The matrix is the principal material in the waste package, and determines in-package chemistry.

In the present analysis, we consider the case for direct disposal of UN spent fuel in Yucca Mountain Repository (YMR). For the case of disposal of solidified HLW resulting from reprocessing of spent UN fuel, previous results for defense HLW (DHLW) vitrified by borosilicate glass are used by assuming dissolution of borosilicate glass is the same for both cases.

For scoping evaluations attempted in this study, a model has been established for dissolution of the matrix material and cumulative release of radionuclides from the matrix to the surrounding environment. While numerical results are shown for matrix dissolution only, radionuclide release can also be evaluated numerically with the model once radionuclide compositions in the matrix are given.

Model

In this study, radionuclides are considered to exist in the environment after released from a failed waste package, and to become environmental impact of the repository. In reality, some radionuclides released from failed packages still exist within engineered barriers such as the drip shield or in the near-field host rock included in the repository region, which could be excluded from repository impact consideration. With this simplification, the mass $\overset{\vee}{M_i}$ of radionuclide i in the environment can be conservatively overestimated.

For the time period between the time of emplacement of the waste packages in the repository ($t = 0$) and the time of waste package failure ($t = $), no radionuclides are assumed to be released into the environment, but within waste packages the radionuclide composition changes with time due to radioactive decay. Therefore, for the mass $\overset{\vee}{M_i}$ of radionuclide i in the environment,

$$\overset{\vee}{M_i} \qquad . \quad (1)$$

For the mass in a single waste package $\overset{\vee}{M_i}$, the governing equation is written as

$$\overset{\vee}{M_i} \qquad (2)$$

subject to $\qquad$. (3)

$\boxed{\times}$ is the decay constant for nuclide i. The time point $t = 0$ is set at the time of waste package emplacement in the repository. All the packages of the same type are placed in the repository at the same time $t = 0$ and fail at the same failure time $\qquad$. $\boxed{\times}$ is the mass of nuclide i in a single package at the time of package emplacement in the repository. The solution for $\boxed{\times}$ is readily available [4].

After the package failure, the balance equations are written as

$$\overline{\qquad} \qquad (4)$$

$$\text{subject to} \qquad , \qquad (5)$$

$$\overline{\qquad} \qquad (6)$$

subject to the value of $\qquad$ obtained by substituting $t = T_f$ in the solution to Error! Reference source not found. **as the initial condition.**

In the last term of Error! Reference source not found. **and** Error! Reference source not found.**, the rate** $\qquad$ **of release from a failed waste package for radionuclide i is included. Note that from physical consideration** $\qquad$ **if and only if** $\boxed{\times}$ **. Once** $\boxed{\times}$ **vanishes, so does** $\qquad$ **.**

Because the YMR consists of a single layer of a waste-package array with groundwater flowing downward perpendicular to the layer, and because the drift tunnels are separated with a sufficiently large distance of 81 m,[5] the release of radionuclides from a failed package is not influenced by adjacent failed waste packages[6]. Therefore, in Error! Reference source not found.**,** $\qquad$ **is multiplied by the total number N of waste packages of the same type in the repository[7].**

Radionuclides are released by waste matrix dissolution either in congruent-release or solubility-limited mode[8].

For the congruent release, the release rate for nuclide i can be written as

$$\qquad , \qquad (7)$$

where $\qquad$ **is the fractional dissolution rate of the matrix, defined as**

[4] M. Benedict, T. H. Pigford, and H. Levi, *Nuclear Chemical Engineering*, Chapter 8, 2nd ed., McGraw-Hill, 1981.

[5] Total System Performance Assessment - Analyses for Disposal of Commercial and DOE Waste Inventories at Yucca Mountain - Input to Final Environmental Impact Statement and Site Suitability Evaluation REV 00 ICN 02, 2001.

[6] J. E. Houseworth, S. Finsterle, and G. S. Bodvarsson, Flow and Transport in the Drift Shadow in a Dual-Continuum Model, *J. Cont. Hydrology*, **62-63**, 133-156, 2003.

[7] J. Ahn, D. Kawasaki, P. L. Chambré, Relationship among Performance of Geologic Repositories, Canister-Array Configuration, and Radionuclide Mass in Waste, *Nuclear Technology*, **126**, 94-112, 2002.

[8] P. L. Chambré, T. H. Pigford, A. Fujita, T. Kanki, A. Kobayashi, H. Lung, D. Ting, Y. Sato, and S. J. Zavoshy, Analytical Performance Models for Geologic Repositories, LBL-14842, Lawrence Berkeley Laboratory, October 1982.

$$\text{(8)}$$

with the dissolution rate of the matrix and the mass of the matrix remaining in a failed package.

For spent UN fuel, the matrix is considered to be UN including isotopes, ^{233}U, ^{234}U, ^{235}U, ^{236}U, and ^{238}U, while most DHLW is solidified by borosilicate glass[Error! Bookmark not defined.]. For UN, and are obtained by considering the mass and dissolution rate of UN in the package, respectively. For DHLW, these are for the mass and dissolution rate of silica. UN and borosilicate glass are assumed to dissolve in the solubility-limited release mode.

For the solubility-limited release, formulae for the rate of steady-state mass transfer by advection and diffusion from the surface of a cylindrical waste matrix were obtained in reference given in footnote Error! Bookmark not defined.. The dissolution rate [mol/yr] of the dissolving species of nuclide i from the surface of the waste matrix was expressed as

$$\text{(9)}$$

_ is the porosity of the surrounding porous rock. [m^2/yr] is the diffusion coefficient of the dissolving chemical species of element e, in which isotope i is included. [kg/m^3] is the solubility allocated for nuclide i. [m] and [m] are the length and the radius of the cylindrical waste package, U [m/yr] the ambient pore velocity of groundwater. is the Peclet number, dimensionless.

The release rate for the solubility-limited release is written as

$$\text{(10)}$$

With , the fractional dissolution rate for the solubility-limited release can be written as

$$\text{(11)}$$

Whether the congruent release Error! Reference source not found. or the solubility-limited release Error! Reference source not found. is applied can be determined by comparing the fractional release rates with . If , then radionuclide i will be released congruently with the matrix dissolution. Otherwise, the nuclide will be released under the solubility-limited release mode. Thus, is formulated for as follows:

$$\text{(12)}$$

where index i is for all nuclides except for those considered as the matrix.

For the solution for the problem given by Error! Reference source not found.**,**
Error! Reference source not found.**,** Error! Reference source not found. **and**
Error! Reference source not found.**, we consider an arbitrary time interval between** and
, for **. Within this time interval, we assume that the fractional dissolution rate**
of the matrix is constant at the value **. Then, the analytical solutions for the**
balance equations have been obtained, with which we have made numerical evaluations for
and **for** **in a stepwise manner.**

Data and Numerical Results

The dissolution rate of the UN was estimated to be approximately 7E-4 g/m^{2}h in de-aerated water at ambient temperature and > 9E-4 g/m^{2}h at 92°C.[9] These values could be significantly reduced if a layer of UO_2 is formed on the surface of UN fuel pellets by exposure to water. Exposure to oxygen also results in the oxidation of a fresh surface of UN.[10] It is well known that UO_2 has low solubility in water.[11] Therefore, a UN sample covered with a UO_2 layer may appear unreactive in water. Such observations were also made in previous experiments.[12, Error! Bookmark not defined.]

Also from literature, for U metal, the dissolution rate was estimated to be ~28 g/m^{2}h in water at 100°C.[13] For U_3Si, it was between 9E-7 and 9E-5 g/m^{2}h at 100°C.[14] Thus, the dissolution rate for UN is much smaller than that for U metal but greater than that of U_3Si.

In YMR, where the host rock is partially saturated with water and in oxidative conditions, UN may have coatings of UO_2, resulting in significantly smaller dissolution rate of UN matrix.

Predicted rates of dissolution of the commercial-spent nuclear fuel (CSNF) were obtained as a function of temperature and pH for the TSPA calculations[15]; at 50°C and pH=7, the dissolution rate is shown to be 2E-4 g/m^{2}h.

With this value, 7,500 kg for the mass of uranium in a CSNF package and the geometrical surface area of the waste matrix is approximately 8 m^2, the time for completion of degradation has been calculated to be 3.8E5 years by the model described in the previous section.

For borosilicate glass in the DHLW, the dissolution rate is reported to be of the same order as the degradation rate of the CSNF fuel.[Error! Bookmark not defined.] The average mass of silica per Co-disposal package is approximately 7,700 kg, which is close to the mass of uranium in the CSNF package. Thus, the dissolution time for the DHLW has been calculated to be 3.9E5 years by the model.

[9] S. Sunder and N. H. Miller, *Corrosion of UN in Water*, AECL-11656, October 1996.

[10] K. Ikawa and K. Taketani, Room Temperature Oxidation of Uranium Nitride Powder, *Journal of Nuclear Science and Technology*, **7(9)**, 433-438, 1970.

[11] D. W. Shoesmith, S. Sunder, and W. H. Hocking, Electrochemistry of UO_2 Nuclear Fuel, VCH Publishers Inc., New York, NY, 297-337, 1994.

[12] S. Sugihara and S. Imoto, Hydrolysis of uranium nitrides, *Journal of Nuclear Science and Technology,* **6**, 237-242, 1969.

[13] W. T. Bourns, *Corrosion testing of uranium silicide fuel specimens,* AECL-2718, 1968.

[14] W. T. Bourns, A literature survey of U_3Si corrosion, AECL-2609, 1967.

[15] Yucca Mountain Science and Engineering Report, US Department of Energy, Office of Civilian Radioactive Waste Management, DOE/RW-0539-1, February 2002. http://www.ocrwm.doe.gov/documents/feis_2/index.htm

From aforementioned comparisons, it may be reasonable to assume that the dissolution rate of UN would be greater than that of UO$_2$ in the YMR environment approximately by one order of magnitude. Assuming that the waste package for UN spent fuel has the same geometrical dimensions as those for the CNSF package, and contains the same mass of uranium, the dissolution time for UN spent fuel package has been calculated to be 3.5E4 years, which is about a factor of 10 smaller than those for CSNF and DHLW.

In this analysis, detailed calculations for radionuclide release and accumulation in the environment have not been made. With results of burn-up calculations for UN fuel, quantitative evaluations for cumulative radionuclide release can be made. If the dissolution time of the UN spent fuel is of the order of a few tens of thousands of years, mass of Pu-239 in the spent fuel would affect the environmental impact from the UN spent fuel disposal significantly.

Summary

The estimate shown in this chapter is subject to many uncertainties and assumptions, and is semi-quantitative. The reported high dissolution rates of UN in water at ~ 92°C indicate that UN is not stable in the hot aqueous environment. The numerical evaluation, based on the assumption that the dissolution rate of UN spent fuel is 10 times greater than those for UO$_2$ and borosilicate glass, indicates that the dissolution of UN spent fuel would complete within the time duration comparable to the half-life of Pu-239.

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